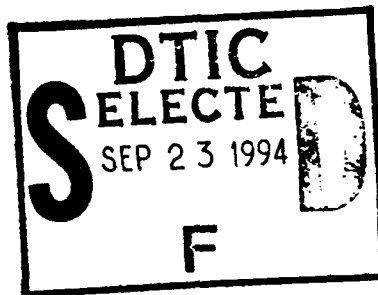


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**MODELING TRIHALOMETHANE
FORMATION POTENTIAL
FROM
WASTEWATER CHLORINATION**

THESIS

Carol A. McCormick, Captain, USAF

AFTT/GEE/ENV/94S-14

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**MODELING TRIHALOMETHANE FORMATION POTENTIAL
FROM WASTEWATER CHLORINATION**

THESIS

**Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology**

Air University

**In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering and Environmental Management**

Carol A. McCormick, B.S.

Captain, USAF

September 1994

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Preface

The purpose of this research was to evaluate and apply analytical models which could be used to determine the trihalomethane formation potential of chlorinated wastewater. This model is needed to assess the potentially detrimental effects chlorination disinfection by-products may have on the receiving bodies of water to which US Air Force facilities discharge their wastewater. This model will also be useful at any wastewater treatment plant which uses chlorine as a disinfectant.

Data was solicited through the use of surveys. All Air Force wastewater treatment plants were solicited to determine the extent of chlorine use, the use of dechlorination units, and to obtain typical wastewater characteristics and disinfection by-products formed. Survey results gave substantial characteristic wastewater data but little disinfection by-product data due to the expense of testing required to obtain the data. Current permits do not require the measurement of trihalomethanes, thus, the extent of trihalomethane emission from AF wastewater treatment plants is unknown.

Three drinking water disinfection by-product models were compared to assess their predictive accuracy versus measured values from data obtained from previous research. I found the models to predict on the high side for typical ranges of wastewater treatment plant data. The model with the least mean squared error was used to develop a range of wastewater treatment plant conditions which could potentially form a harmful amount of THMs.

In finding a valid model for use and in writing this thesis I required the assistance of many wastewater and chemistry experts. I am indebted to my faculty advisor, Dr. Charles Bleckmann, and to my statistics expert, Professor Dan Reynolds. I am deeply indebted to Dr. Larry Burggraf of the AFIT Physics department, without whose chemical know-how this thesis would not have been possible.

Carol A. McCormick

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Abstract

The deletion of federally mandated fecal coliform limits has led many states to review and modify their wastewater disinfection requirements. One issue in analyzing wastewater disinfection is the discharge of potentially carcinogenic halogenated organics formed during the chlorination process. This research investigates the formation of one class of the halogenated organics, the trihalomethanes. The applicability of using drinking water trihalomethane formation models for use with wastewater effluent characteristics is examined. Three models are compared for predictive capability by using measured trihalomethane values from previous research data.

The results show that a previously developed model is applicable for use based on assumptions stated. Results provide environmental managers with worst case predictions for a wide range of wastewater treatment plant (WWTP) parameters. Model predictions indicate that trihalomethane formation from the chlorination of wastewater effluent is typically lower than the US Safe Drinking Water trihalomethane interim standard of 100 ug/L. However, environmental managers should be aware that their WWTP may be forming disinfection by-products.

The worst case model predictions reach, and in certain extreme cases, pass the interim standard of 100 ug/L. This level of trihalomethanes formed is minimized if aeration of the receiving bodies of water occurs. Based on this research, the risk of forming trihalomethanes as disinfection by-products from chlorination do not outweigh the benefits gained from proper chlorine disinfection of wastewater effluent.

MODELING TRIHALOMETHANE FORMATION POTENTIAL FROM WASTEWATER CHLORINATION

1.0 Introduction

Since the early 1970's the United States public has become increasingly interested in the quality of our environment. We found several of our communities had been built atop toxic waste dumps; our sewage dumping had turned many of our rivers and lakes into lifeless water unfit for recreational or drinking water use; and our sunny skies were blocked by clouds of air pollutants. Public concerns and pressure led Congress to begin passing a series of environmentally centered legislation. The Federal Water Pollution Control Act was passed in 1972. Along with a series of amendments, the law is now commonly referred to as the Clean Water Act (CWA). The 1972 statute mandated the US Environmental Protection Agency (USEPA) to set federal standards for effluent quality from industries, set effluent limitations, began an effluent permitting program, set special provisions for toxic substances and oil spills, and set up a grant program to construct publicly owned treatment works (POTW) (Arbuckle, 1993:153). Many of these measures have forced industry and the public sector to drastically improve the quality of our rivers and lakes. Yet, pollutants are still discharged on a daily basis. This research will address the potential formation and hazards of one group of those pollutants, trihalomethanes (THMs).

To ensure the downstream protection of human health, any water discharged from a wastewater treatment plant (WWTP) must be disinfected to prevent the spread

of disease causing (pathogenic) organisms. Waterborne diseases caused by inadequate disinfection of wastewater may be spread through use of the receiving water for: bathing, as a drinking water source, for growing fish or shellfish, or for the irrigation of crops. It was discovered late in the 1800's that chlorinated lime would deodorize sewage and disinfect fecal material from hospitals that was known to contain pathogenic organisms (Singer, 1988:4). Over the past century, chlorination has evolved as the most commonly used method of disinfecting wastewater. The ubiquitous use of chlorine has been due to the relative ease of use, effective disinfecting capabilities and low production cost (Singer, 1988:1). One by-product from the use of chlorine to disinfect wastewater, is the formation of trihalomethanes, as well as many other halogenated organics.

Water in the natural environment is far from pure. Rivers, lakes and wetlands are dynamic systems subject to the inflow and outflow of a myriad of materials produced by natural and anthropogenic sources. These materials react chemically with each other, and with living organisms, particularly bacteria (Manahan, 1991:435). To ensure effective disinfection, to meet the CWA federally mandated secondary treatment standard for fecal coliform bacteria levels, many WWTPs indiscriminately over-chlorinated the wastewater effluent with little thought of the potential effects on fish and other aquatic organisms (WPCF, 1984:2). The residual chlorine remaining in the effluent began having damaging effects on the receiving bodies as the chlorine reacted with non-target organisms and their environment. In the past decade, the detrimental effects of the extensive use of chlorine has become a concern. Two main areas of concern are the toxic effects of chlorinated effluent on aquatic ecosystems and the effects of the formation of potentially carcinogenic halogenated compounds which could contaminate downstream drinking water sources (Singer, 1988:1). In 1976, the fecal coliform limitation was deleted from the CWA and replaced by state mandated

site specific disinfection standards. The limitation was deleted based upon these two undesirable consequences of chlorination practices (Longley, 1986:3).

Concerns over the ubiquitous presence of these halogenated compounds in drinking water sources led to a focus on the particular group of volatile halogenated organic compounds known as the trihalomethanes (THMs) (Trussell, 1978:604). One of the THMs, chloroform, is a suspected human carcinogen. In 1979, concerns over adverse health effects led the USEPA to set a maximum contaminant level (MCL) of 0.10 mg/l for THMs in drinking water (Singer, 1988:2). Recent movements by the Clinton administration include a proposal in the revised clean water bill to examine the health effects of chlorine and chlorinated compounds and possibly restrict or prohibit the use of chlorine and related compounds (Cushman, 1994).

1.1 Objectives of the Research

Chlorinating wastewater effluent for disinfection leads to the formation of halogenated compounds. One class of these compounds, THMs, are known animal and suspected human carcinogens. Research into the human health and ecological risks of THMs is ongoing. The goal of this research is to propose a model to identify THMs formation potential from chlorinating wastewater.

Objectives of the Research

- A. Define the processes and components involved in the formation of trihalomethanes as they occur from chlorinating wastewater effluent.
- B. Review and analyze significant prior research on the formation and hazards of trihalomethanes.

- C. Define an analytical model to predict treatment plant total trihalomethane formation potential.
- D. Model the formation of trihalomethanes from the chlorination of wastewater using a WWTP's effluent characteristics for model inputs.
- E. Analyze the ecological risk posed by these compounds in wastewater effluent.

1.2 Department Of Defense: Justification For Research

1.2.1 US Air Force Use Of Chlorine Disinfection. The US Air Force currently operates fifty-nine WWTPs releasing a total of over 35 Million Gallons per Day (MGD) of effluent. Those WWTPs located in the continental United States must comply with state mandated coliform limitations for their effluent. The Air Force currently uses chlorination for disinfection at twenty-eight of these WWTPs. Only thirteen of the plants dechlorinate the disinfected effluent (See Table 1). Therefore, fifteen plants release chlorinated effluent directly into bodies of water which have a potential for harm if THMs are formed. The dechlorination process involves the use of a chemical additive, usually sulfur dioxide (SO_2), to remove any residual chlorine from the effluent. This process helps to diminish the toxicity of the effluent in general but does not eliminate any THMs that are formed during the chlorine contact duration. Many states are currently considering mandating dechlorination or alternative disinfection methods based upon public concerns and upon the impending stricter regulations on the use and discharge of chlorine. The Air Force should therefore be considering the cost benefits of dechlorination versus the use of alternative disinfection

Table 1 Air Force Wastewater Treatment Plants
(Research Surveys (Appendix A) and Geo-Marine, 1993:5-55).

<u>Air Force Base</u>	<u>Treatment</u>	<u>Disinfection</u>	<u>Type of Dechlor</u>	<u>Chlorine Use Per Day</u>	<u>Max Flow</u>	<u>Discharge To</u>
Air Force Academy	Tertiary	Chlorination		—	4.5 MGD	Irrigation Reservoirs
Arnold, TN	Activated Sludge	Chlorination		5 lbs	0.232 MGD	Roland Ditch
Arnold, TN	Package Plant	Chlorination		—	.03 MGD	Woods Reservoir
Beale, CA	Trickling Filter	Chlor/Dechlor	SO ₂	72 lbs	5.0 MGD	Irrigation and Hutchison Crk
Cannon, NM	Oxidation Pond	None		—	—	Irrigation / Playa Lake
Cape Canaveral, FL	Trickling Filter	Chlor/Dechlor	—	—	0.49 MGD	Evaporation / Percolation
Cape Canaveral, FL	15 Package Plants					
Castle, CA	Trickling Filter	Chlor/Dechlor	SO ₂	—	1 MGD	Canal Creek
Columbus, MS	Trickling Filter	Chlorination		35 lbs	0.436	Tombigbee Waterway
Eglin, FL	Activated Sludge	Chlorination		—	1.0 MGD	Evaporation / Percolation
Eglin, FL	Activated Sludge	Chlorination		—	1.5 MGD	Evaporation / Percolation
Eielson, AK	Aerated Lagoon	Chlorination		20 lbs	1.5 MGD	Evaporation / Percolation
Ellsworth, SD	Trickling Filter	Chlor/Dechlor	SO ₂	40 lbs	2.4 MGD	Boxelder Creek / Irrigation
Falcon, CO	Aerated Lagoon	Chlorination		—	0.153 MGD	Infiltration Basins
Gila Bend ARS, AZ	Oxidation Lagoon	None		—	0.05 MGD	Evaporation / Percolation
Grand Forks, ND	Oxidation Lagoon	None		—	1 MGD	Kelly Slough
Grissom, IL	Activated Sludge	Chlorination		—	2.0 MGD	Pike Creek
Holloman, NM	Oxidation Ponds	None		—	—	Evaporation / playa lake
Hurlbert Fld, FL	Primary	Chlor/Dechlor	SO ₂	30 lbs	1.0 MGD	Wetlands
King Salmon, AK	Aerated Lagoon	Chlor/Dechlor	—	—	—	King Salmon River
Lake, AZ	Tertiary	Ultraviolet		—	1.2 MGD	Agua Fria River / Irrigation
MacDill, FL	Activated Sludge	Chlorination		—	1.2 MGD	Irrigation of golf courses
MacDill, FL	No Data on Second Plant					
March, CA	Trickling Filter	Chlorination		55 lbs	0.75 MGD	Turf Irrigation
Martinsburg ANG, WV	Activated Sludge	Chlor/Dechlor	—	—	0.48 MGD	Opquor Creek
McEntire ANG, SC	Tertiary	Chlor/Dechlor	—	—	—	—
McGuire, NJ	Trickling Filter	Chlor/Dechlor	—	—	1.5 MGD	South Run Creek
Minot, ND	Oxidation Pond	None		—	—	Egg Creek
Moody, GA	Trickling Filter	Chlorination		—	2.0 MGD	Beatty Creek
New Boston ARS	Package Plant	—		—	—	—
Patrick, FL	Secondary	Chlor/Dechlor	SO ₂	55 lbs	1.0 MGD	Future cnct to Cocoa Beach
Phelps Collins ANG, MI	Activated Sludge	—		—	0.1 MGD	Thunder Bay River
Reese, TX	Secondary	Chlorination		25 lbs	0.5 MGD	Turf Irrigation
Robins, GA #1	Trickling Filter	—		—	—	Ocnulgee River
Robins, GA #2	Chemical Precipitation	—		—	0.46 MGD	Ocnulgee River
Robins, GA #3	Chemical Precipitation	Chlorination		—	—	Ocnulgee River
Scott, IL	Trickling Filter	Chlor/Dechlor	—	—	—	—
Shaw, SC	Secondary	Chlor/Dechlor	SO ₂	13 lbs	1.2 MGD	Beech Crk to Wateree Rvr
Sheppard, TX	Sanitary-Secondary	Chlorination		—	—	—
Sheppard, TX	Industrial-Secondary	—		—	—	—
Tinker, OK	Sanitary - Secondary	None		—	0.7 MGD	Soldier Creek
Tinker, OK	Industrial - Tertiary	None		—	1.2 MGD	Soldier Creek
Vandenberg, CA	Package Plant	—		—	—	—
Volk Field, WI	Oxidation Lagoon	Chlor/Dechlor	—	—	0.42 MGD	Lemonwear River
Whiteman, MO	Trickling Filter	—	—	—	1.26 MGD	Brewer Branch

— Indicates data unavailable

methods. Current research into these cost benefits is being performed in a related thesis by Captain Dave Piech. Based upon upcoming reauthorization of the CWA and the tougher standards that are pending for chlorine residuals and chlorine disinfectant by-products toxicity, the Air Force should also be considering the disinfection by-products formed at Air Force WWTPs. This research investigates the formation of one group of these by-products, THMs, and the detrimental effects these by-products may be causing to the receiving bodies of water.

1.2.2 Potential For Water Re-use. Twenty Air Force WWTPs discharge to creeks or rivers which eventually may be re-used as drinking water sources. Tinker Air Force Base (AFB) in Oklahoma discharges to East Soldier Creek which is categorized by USEPA as a warm water aquatic/primary recreation class river (Geo-Marine, 1993:53). East Soldier Creek then discharges into the North Canadian River. This large river runs nearby downtown Oklahoma city. Recreational use is constant, and the potential of surface water extraction for drinking water is apparent. The extensive re-use of reclaimed water necessitates the production of wastewater effluent that will meet potable water standards wherever human contact may occur. Another example is the discharge of Shaw AFB in South Carolina which enters the Wateree River and then flows through the city of Sumter. Many states are currently considering lowering the chlorine residual levels allowed by current discharge permits based on toxicity of the disinfection by-products and the potential for water re-use. Since the Air Force must abide by all state mandated discharge limits, the Air Force should be considering the amount of disinfection by-products which we actually produce at our WWTPs.

2.0 Literature Review And Theoretical Considerations

2.1 Wastewater Chlorination

2.1.1 History. In ancient times, people began collecting rain and storm water to support the growing cities. It was not until the mid 1800s, however, that the collection of wastewater became common in Europe. The practice of systematic treatment of wastewater began in the late 1800s early 1900s, brought about in part by the limited size of the receiving bodies of water accessible to Europeans. The relationship of untreated wastewater to disease was beginning to be understood. Originally, disease was thought to spread through odors and therefore the control of odors would prevent disease. To control the odors, chlorine was used as a deodorant without the understanding of its germicidal capabilities (White, 1992:479). The earliest use of chlorine as a deodorant was documented in 1854 when the Royal Sewage Commission used chloride of lime to deodorize London sewage (White, 1992:479).

The major disease relationship breakthrough of Koch and Pasteur's germ theory in the late 1800s created a new age of sanitation practices. It was now understood that certain pathogens caused certain diseases. Chlorine was first used as a disinfectant in 1879, when William Soper of England treated the feces of typhoid patients with chlorinated lime before disposal in the sewage system (White, 1992:479).

Here in the United States, wastewater treatment and disposal was not of great concern until the late 1800s. Previous to this time, our discharges had not caused a noticeable aesthetic change in our waters due to the large volume of the receiving bodies. More advanced methods of treatment were developed as nuisance and health conditions worsened (Tchobanoglous, 1991:2). To counter a waterborne typhoid

epidemic in 1894, chlorine was used on a plant wide basis to disinfect the New York City water supply coming from the Brewster, New York, water plant (White, 1992:479). Since the development of metering and supply systems for chlorine gas, the use of chlorine to disinfect wastewater has grown tremendously.

2.1.2 Wide Use of Chlorine for Effluent Disinfection. Chlorine is added to the hydrosphere in vast amounts through many different anthropogenic processes. Ten percent of the world's chlorine production is by one company, Dow Chemical, at a rate of approximately five million tons yearly. Over 10,000 different chlorine compounds are produced to manufacture the goods we use daily (Amato, 1994:152). As of 1958, 30% of all WWTPs in the US, over 2200 plants, were equipped with chlorination equipment (White, 1992:480). As a result of the 1970 Water Pollution Control Act, almost all treatment plants are now subject to some form of disinfection. The majority of WWTPs requiring disinfection currently use some form of chlorination. Based on the health hazards and environmental concerns of chlorination, many of the plants are installing alternative disinfection processes such as UV irradiation or ozonation. Over 400 facilities have been designed for chlorination/dechlorination with approximately 50% of those facilities in use as of 1986 (USEPA, 1986:9).

2.1.3 Wastewater Treatment Process. Disinfection is only a part of the wastewater treatment process. Current practice includes the use of physical and chemical methods to remove contaminants from the influent. Those processes which involve physical removal methods are known as unit operations. Those methods which involve a chemical process to change the wastewater characteristics are known as unit processes. These two types of removal strategies are combined together to provide what is known as primary, secondary, and tertiary treatment. Primary treatment usually

consists of screening and sedimentation to remove floating and settleable solids from the wastewater. In secondary treatment, chemical and biological processes are used to remove organic matter from the wastewater. Tertiary treatment is needed if the effluent contains other constituents such as nitrogen or phosphorous that have not been sufficiently reduced through secondary treatment. A combination of chemical and physical operations could also be used during this phase to reduce the amount of heavy metals or other pollutants from the effluent. Lastly, the effluent is disinfected to reduce the amount of pathogenic organisms discharged to receiving waters.

(Tchobanoglous, 1991:2,3)

2.2 Chlorination Chemistry

2.2.1 Introduction. To understand how trihalomethanes are formed, the basics of chlorine chemistry must first be understood. Chlorine is an element of the halogen family. The halogens are strong oxidants and are highly reactive (Manahan, 1991:504). Chlorine is never found uncombined in nature, it exists only as the negative chloride ion (valence -1) combined with other elements in the form of soluble chlorides. White estimates that 0.15% of the earth's crust is made up of common chlorides such as salt (NaCl) and sylvite (KCl).

Chlorine's properties differ greatly depending upon its physical state. Chlorine gas is a pungent-smelling, greenish-yellow gas that is extremely irritating to mucous membranes. In the gaseous state, it is about two and one-half times as heavy as air and readily sinks to the ground when released. Chlorine gas is soluble in water and has a bleaching effect on many forms of natural fibers. Liquid chlorine is formed by compressing chlorine gas, one volume of liquid yielding approximately 450 volumes of

gas. The yellowish amber liquid volatilizes violently when depressurized (White, 1992:1,2), one of the many hazards to WWTP workers.

2.2.2 Chemistry of Free Chlorine. Chlorine's high reactivity and oxidizing capacity are caused by the fundamental properties of chlorine. Chlorine's high electron affinity tends to draw electrons towards it, resulting in high reactivity with other atoms. It is an electron acceptor. Chlorine's oxidizing capacity is based on fundamental oxidation-reduction reactivity. Oxidation-reduction reactions are those involving a change of oxidation state of the reactants. These reactions can be visualized as the transfer of electrons from one species to another. For example, chlorine may be added to water in three common ways: as chlorine gas (Cl_2), as sodium hypochlorite (NaOCl), and as calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). When added to water as gas, it rapidly hydrolyzes to produce hypochlorous acid (HOCl) according to the following reaction:



The hydrogen is oxidized and the chlorine gas is reduced (Manahan, 1991:67,209). At a typical 18°C , hydrolysis occurs in a few tenths of a second. Only a few seconds are needed for complete hydrolysis if the temperature decreases to 0°C . At almost every collision of the chlorine molecule and the hydroxyl ion (OH^-) this reaction occurs. The weak hypochlorous acid then easily dissociates into hypochlorite ions (OCl^-) and hydrogen ions (H^+):

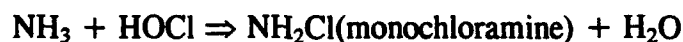


Hypochlorous acid is the most effective germicide of all the chlorine compounds except possibly chlorine dioxide (White, 1992:185,187). Singer reported in 1988 that Snoeyink and Jenkins found " HOCl to be 80 to 100 times more effective than OCl^- at killing *E. coli*". This effectiveness is a result of HOCl 's strong oxidative capacity.

When chlorine exists as either hypochlorous acid or as the hypochlorite ion, it is referred to as free chlorine or free available chlorine (Singer, 1988:6).

Free available chlorine not only acts as a germicide but combines with other organic and inorganic compounds present in water and wastewater. The compounds compete for free available chlorine and sometimes lead to lessened germicidal effectiveness. One of the main competing reactions, when chlorine enters wastewater, is its reaction with ammonia.

2.2.3 Reactions With Ammonia. When ammonia (NH_3) is present in wastewater, three types of chloramines are formed, depending upon pH, temperature, contact time, and molar ratios, according to the following competing reactions:



These three chloramines are referred to as combined chlorine and are oxidizing agents that aid in the disinfection capability of free chlorine. The rate of these reactions can best be shown by a theoretical breakpoint curve as shown in Figure 1.

At chlorine to ammonia molar ratios of 0 to 1, the combined chlorine residual reaches a maximum due to the formation of monochloramine (between A and B of Figure 1). The combined chlorine residual decreases as the ratio grows larger than one. The unstable formation of dichloramine occurs in this region (between B and the breakpoint). At the "breakpoint" of the curve, the chlorine to ammonia usually ranges from ratio reaches 1.5 to 1. All original ammonia has reacted and converted to other compounds. Past the "breakpoint" any additional chlorine remains as free available chlorine (Singer, 1988:7 and White, 1992:196-198). This theoretical curve is for an

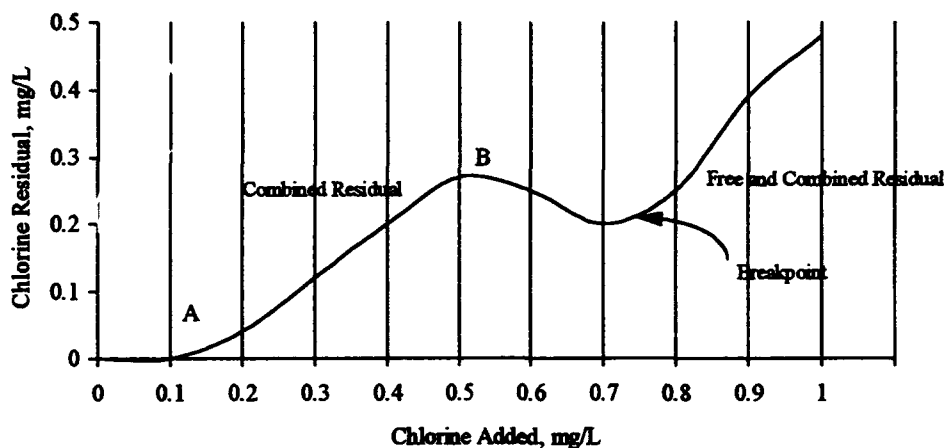


Figure 1 Theoretical Breakpoint Curve (Tchobanoglous, 1991:334).

ideal chlorine-ammonia system where no impurities compete for chlorine. The shape of the curve is affected by contact time, pH, temperature, and the concentrations of chlorine and ammonia. The “breakpoint” curve will be different for each chlorination process based on all dependent factors as well as the presence of compounds other than ammonia. Common wastewater disinfection is to practice “breakpoint” chlorination so chlorine residual is minimal. A “rule of thumb” in disinfection practice is 10 parts by weight of chlorine to one part of ammonia is required to reach the “breakpoint” (2:1 on a molar ratio basis) (Singer, 1988:8 and White, 1992:208).

2.2.4 Reactions With Organic Compounds. The reactions of chlorine with organic compounds in water are varied and complex, depending upon the water characteristics, the chlorine dose, and the physical state of the added chlorine (Abarnou and Moissac, 1992:176). Reactions with organic compounds can be divided up into two groups based on whether the reaction mechanism is oxidation or substitution (Johnson, 1986:160). Oxidation reactions are the most prevalent reactions. These

reactions occur when free available chlorine oxidizes organic compounds. The oxidative capacity of chlorine is lost and any chlorine added past the equilibrium point is found as the unreactive non-toxic chloride ion (Singer, 1988:10). In saline water, bromide is instantaneously oxidized into bromine, which gives rise to bromamines. This first group of reactions is responsible for the efficiency of chlorine disinfection as well as for toxicity towards non-targeted organisms. Toxicity eventually disappears as the oxidizing capacity is lost or transformed from one chemical entity to another (Abarnou, 1992:176).

The second reaction results in the formation of halogenated organic derivatives which are of interest in this study. The reaction occurs when chlorine atoms are substituted for some other atom present in the organic compound (Morrison, 1992:43). These substitutive reactions are significant because:

- (a) the end products of these reactions may be numerous ,
- (b) they persist in the environment longer than the first group of compounds
(Abarnou, 1992:191),
- (c) they may present carcinogenic risk.

This research will focus on modeling the formation of THMs, one group of these halogenated organic derivatives.

2.3 Formation of Chlorinated Organic Compounds During Wastewater Chlorination

Halogenated organic compounds, including the THMs, are formed during wastewater chlorination and also by the reaction of free chlorine residual in chlorinated wastewater with organics in the receiving surface waters. THMs were first identified as a potential pollution problem by Rook in 1974. In the investigation, halogenated

organic compounds (also known as haloforms) were found at significant levels immediately following chlorination of a natural water source. Principal among the haloforms found were the THMs, especially chloroform. Haloforms have the general formula CHX_3 , where X denotes a halogen (fluorine, chlorine, bromine, iodine). The currently regulated THMs are chloroform (CHCl_3), bromodichloromethane (BrCHCl_2), dibromochloromethane (Br_2CHCl), and bromoform (CHBr_3) (Gilbert, 1992:136). THMs are formed through alternate hydrolysis and halogenation steps, with the first ionization steps being rate determining (Trussell, 1978:605). An example of the haloform reaction in chlorinated wastewater is given in Figure 2. The precursors needed for this reaction are generally classed as aquatic humic materials (Johnson, 1986:159). Table 2 summarizes the sources of these precursors.

Table 2 THM Precursors (Johnson, 1986:158)

<i>Source</i>	<i>Examples of Precursors</i>
Plants	Fulvic and humic acid degradation products (resorcinol, vanillic acid, syringic acid, 3,5-dihydroxybenzoic acid) Plant pigments (chlorophyll, phloroacetophenone)
Algae	Algal biomass Amino Acids and pyrimidines (tryptophan, proline, uracil) Extracellular exudates Proteins
Industry	Effluents (phenols)

THMs can be easily determined using gas chromatography and a sensitive detector such as a flame-ionization detector. *Standard Methods for the Examination of Water and Wastewater, 18th Ed.* gives several methods which are accepted under regulatory scrutiny. Liquid-liquid extraction gas chromatograph is highly sensitive and very precise; purge and trap gas chromatograph/mass spectrometric can detect THMs along with a wide range of other compounds; purge and trap GC methods with similar

target compounds are also as effective to detect THMs (Franson, 1992:6-61). Method choice depends on equipment availability and operator choice. These methods need to be followed and documented to ensure data from different investigations are valid.

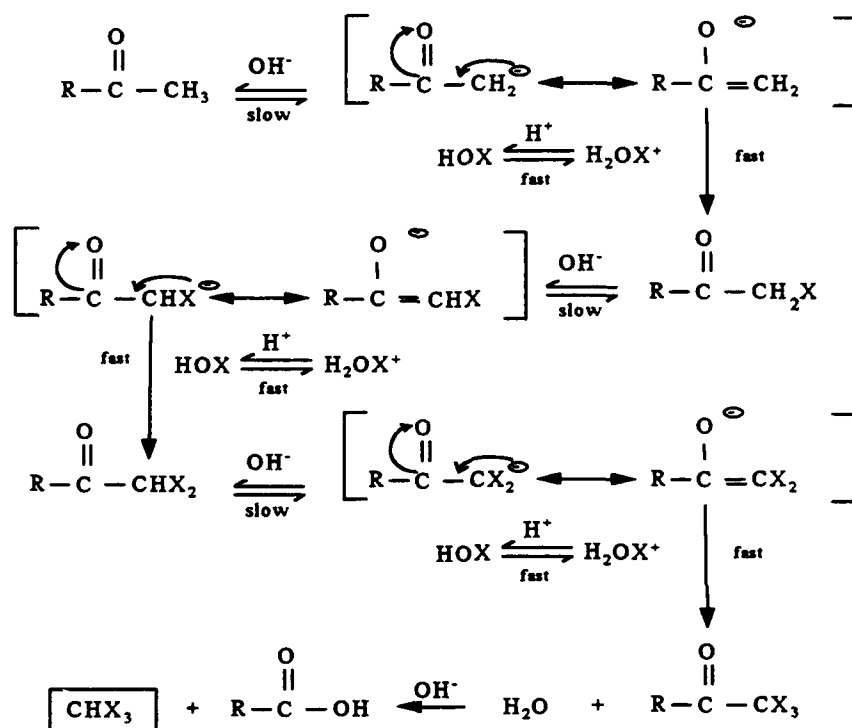


Figure 2 Haloform Reaction Pathway (Trussell, 1978:607).

THM formation is ubiquitous in part due to the amount of readily available precursor compounds, humics that are almost always naturally present in water (See Table 2). Factors which affect the THM formation kinetics include: pH, temperature, level of precursor organics, and level of chlorine dose. THM formation increases with increased temperature and pH, increased level of precursors, and increased chlorine dose (Johnson, 1986:159). Average concentrations of regulated THMs found in municipal wastewater following secondary biological treatment ranged from 1.5 ug/L to 13.3 ug/L (Ram, 1990:129). Treatment plants studied were Washington DC,

Orange County, Phoenix, Denver, and Palo Alto. The presence of the THMs prior to the chlorination process at these plants indicates that they are formed by a variety of industrial and commercial activities as well as the chlorination of drinking water. The additional chlorination of the wastewater then adds to the amount of THMs discharged to surface waters. The amount of THM production is not the only factor which causes concern. Once the THMs are produced, they are persistent in aqueous environments. The half-life of the halomethanes in the aqueous environment depends upon the rate of aeration and on the stability of the haloform. As the halogen bond energies decrease with descending order from chlorine to iodine, the stability of the halomethanes with similar number of halogens can be expected to decrease also (NRC, 1978:40). Therefore, chloroform is expected to be the most stable of the tri-halogenated haloforms. Chloroform was found to have a half-life of 15 months in a sealed aqueous system at 25° C (NRC, 1978:38). It was concluded that hydrolysis was the likely degradation mechanism. The THMs quickly volatilize if exposed to the atmosphere, so in most receiving bodies of water, the rate of aeration will determine how quickly the THMs are degraded if they are not removed through treatment. Air stripping combined with activated carbon treatment is currently the most effective means of removing THMs from a water source (Ram, 1990:132).

It can be seen that using chlorine to disinfect wastewater forms additional toxic compounds which are released into the hydrosphere. The disadvantages of using chlorine as a wastewater disinfectant include: demonstrated toxicity to organisms and the formation of chlorinated organic compounds. A chloroform concentration of 12.1 ug/L was found as an average for purified chlorinated wastewater by Beller in 1974 (Abarnou, 1992:181). Compounds such as chloroform may be carcinogenic and can seriously impact downstream public water supplies (Longley, 1986:5). The toxicity of chlorine residuals and halogenated organics will be further discussed in section 2.4. If

viable alternatives are available, is it important to stop using chlorine as a disinfectant thereby minimizing the amount of disinfection by-products formed and the risk to the environment and to human health? The many public outcries heard recently concerning the damaging effects of chlorine will be discussed in section 2.5.

2.4 Toxicity of Chlorine Residuals and Halogenated Organic Compounds

Early investigations into the toxicity of chlorine and its derivatives focused on free available and combined chlorine with little concern for the possible toxicity of disinfection by-products (DBPs). It was reported by Singer (1988:13) that Wolfe surmised in 1984 that a measure of total residual chlorine present after a chlorination process would be sufficient to express the relative toxicity of a water. This method of measuring toxicity may not be sufficient to account for the toxicity of DBPs. The toxicity of an effluent is caused in part by the oxidizing capacity of any free available chlorine residual. The free chlorine acts as a biocide by altering the permeability of a cell, damaging cellular nucleic acids and inactivating viruses by damaging the viral protein coating or causing nucleic acid mutations (Longley, 1986:5). Many studies have been done since the early 1980s to establish that not only are residual chlorine compounds toxic, but the halogenated organic compounds formed during chlorination are also toxic. The following two sections briefly describe selected studies.

2.4.1 Laboratory Investigations. The use of toxicological indices for regulatory and management purposes became widespread in the late 1940's when these methods appeared in publications by the American Society for Testing and Materials (Cairns, 1987:2). Most of the first indices used were single species laboratory toxicity tests

using fish. Findings were then used to make assumptions as to the toxicity of the compound to humans. In recent years the toxicity of compounds towards plant life has gained precedence as more and more pollution is released to the environment. This section covers both plant and animal studies.

2.4.1.1 Toxicity Studies on Animals. Toxicity of chlorine residuals to aquatic organisms is well documented. The investigation of the effects of chlorinated effluents began during the late 1960s due to public concern. The USEPA released the results of two such major studies in 1976 and 1977. Singer reports that the Ward study tested a wide range of freshwater fish species as effected by completely domestic activated sludge effluent. Most of the pertinent laboratory investigations to test WWTP effluent have been performed using the continuous flow bioassay technique. This techniques involves creating an artificial stream as the test bed and continuously flowing contaminant past the test species. Results from Ward's tests showed that chlorinated effluent was acutely toxic to all species tested with 96 hr TL_{50}^* values ranging from 0.045 mg/l to 0.278 mg/l of total residual chlorine in the effluent. Dechlorinated effluents showed little if any acute toxicity (Singer, 1988:13). Abarnou and Moissec (1992) provide an overview of results observed in laboratory tests. Overall, younger development stages of species are more sensitive than adults. Eggs, however, possess higher resistance to oxidants because of their membrane shells. Lethal concentration of chlorine residual range between 0.01 and 0.1 mg/l for the most sensitive species (Abarnou, 1992:185). In general, most oxidants like chlorine and ozone are identified irritants to both freshwater and saltwater fish species.

* TL_{50} = Tolerance Limit: This means that 50 percent of the fish subjected to the flow for 96 hours will die.

Investigations into the toxicity of chlorinated effluents led to research of the effects of individual halogenated compounds. The acute and chronic toxicity of these compounds is documented by the USEPA in the Ambient Water Quality Criteria series. The USEPA conducts scientific assessments of compounds through the use of accepted toxicological testing methods, such as the TL_{50} test described earlier. The criteria information for trihalomethanes is divided between two Ambient Water Quality Criteria documents, one specifically for chloroform and one for the halomethanes in general. The data for chloroform indicates that acute toxicity to freshwater aquatic life occurs at concentrations as low as 28,900 ug/L to *Daphnia magna* and would occur at lower concentrations among species that are more sensitive (USEPA, 1980:B-3). Chronic toxicity was tested for a 27 day lethal concentration that would kill 50% (LC_{50}) of embryo-larval stage rainbow trout. Toxicity occurred at concentrations as low as 1,240 ug/L, and could occur at lower concentrations for species or other stages of the life cycle that are more sensitive than the earliest life cycle stage of the rainbow trout (USEPA, 1980:B-2). Bluegill fish bioconcentrated chloroform by a factor of 6 times the exposure and the tissue half-life of the accumulation was less than a day. This degree of bioconcentration and short biological half-life suggest that chloroform residues would not be an environmental hazard to consumers of aquatic life (USEPA, 1980:B-2). This suggests that the only hazard to human health from chloroform formed from wastewater disinfection is by direct ingestion of polluted water. Therefore, the formation of chloroform from the chlorination of wastewater could only affect human health if the water was used for recreation or re-used as a drinking water source. The water re-use issue is an important part of the decision to minimize DBPs from wastewater disinfection.

Criteria for the THMs other than chloroform are also published. The Ambient Water Quality Criteria for halomethanes includes criteria for bromoform and

bromodichloromethane. They state that although acute toxicity data is limited, generalizations can be made about compounds in the halomethane class based on available data. The 96-hour LC₅₀ acute toxicity to bluegill occurs at concentrations of 29,300 ug/L for bromoform and at 11,000 ug/L for methyl bromide. Based on these findings they set the criteria at the lower for freshwater aquatic life because no life cycle or embryo-larval tests have been conducted using any halomethane other than chloroform. Therefore, the current criteria guideline used is the chloroform guideline given previously. These criteria values are merely guidelines given to the states by the EPA. Their regulatory influence will be discussed in section 2.5.

A discussion of toxicity is not complete without addressing the human health effects a toxic compound may have. The proposed human health risk of THMs has been presented by the National Cancer Institute (NCI). THMs are currently listed by the NCI as proven animal carcinogens and suspected human carcinogens. They base their findings on their 1976 report showing that high doses of chloroform may cause cancer in rats (NCI, 1976). Based on that publication, the Food and Drug Administration banned the use of chloroform in food preparation and the EPA set interim THM concentration limits for public drinking water supplies in 1979 at 100 ug/l (Trussell, 1978:604 and Singer, 1988:10).

A recent paper by Larson, Wolf and Butterworth in the *Journal of Fundamental Applied Toxicology* questions the hazards of chloroform and the NCI experiment that "proved" carcinogenicity (Abelson, 1994:183). Larson *et al* conducted tests similar to those on which the EPA bases the chloroform ban. In contrast to the EPA tests, where a chloroform and corn oil mixture was fed by direct gavage ingestion, causing the development of stomach tumors in the mice; Larson administered the chloroform to the mice in their drinking water. Results showed that even at high levels of chloroform in the drinking water, there were practically no tumors in the mice (Abelson, 1994:183).

The toxicity of chloroform to humans currently being disputed and is therefore uncertain.

2.4.1.2 Toxicity Studies on Plant Life. The USEPA uses two indicators to determine individual compound's toxicity to plant life. The first indicator is a test of the level of chlorophyll *a* in the freshwater alga *Selenastrum capricornutum*. The second indicator is the number of cells of the same alga. The bromoform 96-hour exposure concentration that would effect 50% of the population (EC_{50}) with a reduction in chlorophyll *a* is given as 112,000 ug/l and the EC_{50} for a decrease in cell mass was 116,000 ug/L (USEPA, 1980a:B-3). Freshwater alga criteria data on the other THMs has not been documented to date.

When the general class of chlorine residuals and chlorinated organics (including THMs) is considered, the effects on plant life become much more devastating than the chlorophyll *a* and cell numbers tests for bromoform indicate. The effects chlorine residuals have had on ecosystems has been investigated through the use of microbial indicators. The use of microbial indicators to determine ecosystem responses to toxic pollutants has been pioneered by Dr. John Cairns and Dr. James Pratt, both with Pennsylvania State University, within the past ten years. An Air Force Office of Scientific Research project was completed in 1988 addressing the structural and functional responses of microcosms to perturbations in aquatic ecosystems. Cairns *et al* used laboratory and field testing methodologies to compare stressors. The laboratory microcosm test used a flow through system with continuous flow of sodium hypochlorite across a microbial community developed on a polyurethane foam substrate (Cairns, 1988:D3-4). The increasing duration of chlorine exposure led to fewer and fewer species on the substrate as compared to controls. Algal biomass was reduced by half after 28 days with a chlorine residual of only 2.1 ug/L. This data suggests that

USEPA's current recommendation for total residual chlorine of 11 µg/L will not protect microbial communities against massive loss of biomass and species diversity (Cairns, 1987:7). Continuous exposure of microbial communities to even very low levels of chlorine may adversely effect them (Cairns, 1988:D-12).

2.4.2 Field Investigations. The use of field investigations is not as prevalent as the use of laboratory experiments. Controls are harder to maintain, conditions are always changing, and results are difficult to interpret. The investigations discussed here are attempts to use the natural environment to monitor changes. They are not simply lab experiments which have been adapted to a field environment. In this way, researchers are beginning to understand more about the dynamics of aquatic environments and the effects of pollution on them.

2.4.2.1 Ecotoxicological Studies. Ecological risk can be defined as the probability of observing a specified effect as the result of toxic chemical exposure (Bartell, 1992:108). An ecological risk can affect the processes, diversity, reproduction rates, and quality of populations of an ecosystem. A disruption of ecosystem parameters can have many effects including reduced biomass, reduced species diversity, species extinction, and propagation of less desirable species. Reduced diversity is caused by avoidance behavior, by mobile species leaving the effected area, and/or by the death of sensitive species. Avoidance responses eventually lead to the loss of habitat in the case of continuous discharges such as chlorinated cooling tower waters or chlorinated effluents (Abarnou, 1992:189). An ecosystem can range from a single microbial community, to an entire watershed, or more. The ecological risk assessment process involves the selection of an indicator species and biological monitoring of that species to determine the "health" of the ecosystem.

Cumulative effects of other risk elements and uncertainties complicate the assessment. For purposes of this research, the risk assessment process need not be explained. (The most recent ecological risk assessment practices are explained in Cothorn (1993).)

One example of an ecosystem toxicity experiment is the outdoor enclosure tests performed by Cairns *et al* in 1988. The researchers brought their efforts on the toxicity of chlorine residuals and DBPs to a field investigation through the use of outdoor enclosure tests. Knowing the toxicity of chlorine, the tests were meant to measure precise levels of residual which cause ecosystem harm. The tests were performed in 130 L polyethylene bags floated in Douglas Lake, Michigan in July 1986. Five nominal chlorine concentrations and a control were tested in triplicate (Cairns, 1988:D-6). The bags were kept afloat, open at the top to expose contents to light, wave action, rain, and air, and the nominal concentrations of chlorine were added daily to the benthic sediment and alga communities which were established in the bags. Initial concentrations that were tested were 10, 30, 100, 300, and 1000 ug/L. Rainfall and exposure diluted the chlorine residual in all enclosures. At only a concentration of 24 ug/L, protozoan colonization rate was significantly reduced (Cairns, 1988:D-11). In the enclosures with the two highest concentrations, 79 and 261 ug/L, algal biomass and species numbers were significantly reduced when compared to controls (Cairns, 1988:D-13). Measurements of DBPs were not taken. Although test results as exact as laboratory measurements could not be obtained through this field experiment, results indicate that exposure to very low levels of residual chlorine can have significant effects on aquatic life.

2.4.2.2 Biological Effects. The biological effects produced by water chlorination on marine organisms has been researched in many countries. Many investigations of WWTP effluents in this country have been prompted by major fish

kills. White reports that a major kill on the Sacramento River prompted an investigation using an in situ static bioassay. All the King Salmon fry below the waste plume died within a captive (kept within a cage type enclosure) 14 hour period of exposure. All fry held upstream survived. Total chlorine residuals were measured from 0.2 mg/l to 0.3 mg/l during the test period. It was assumed that the fish kill was caused by the effluent toxicity, mainly the chlorine residual (White, 1992:581).

Sub-lethal effects include decrease in reproductive potential, growth reduction, irritation of tissues, and disruption of cellular structure among many others. Abarnou and Miossec provide a comprehensive summary of sublethal toxicity tests performed from 1973 to 1983. Overall, growth reduction was observed regardless of the species of animal or plant. Eggs displayed development impairment. A loss of sperm mobility and viability decreased reproductive potential. Photosynthesis and respiration deteriorated in plant species. Gill tissues deteriorated causing an imbalance of gaseous exchanges in fish. The resulting liver hyperactivity lead to degeneration of the liver tissue. Behavioral responses such as avoidance were also observed (Abarnou, 1992:186).

2.5 Current Regulations

The EPA has not yet required that states include chlorine in their non-priority pollutant programs, but as of 1986, approximately 15 states had taken steps to develop specific criteria for determining the impact and adverse effects of chlorine on aquatic life (USEPA, 1986:15). The Ambient Water Quality Criteria document series published by the USEPA (referred to earlier) gives the states toxicity guidelines to ensure human health and ecosystem protection based on specific pollutants. These

criteria become regulated maximum acceptable levels of a pollutant when they are adopted as the state's water quality standards under section 303 of the Clean Water Act. In many situations, states may adjust the water quality standards to reflect local environmental conditions and human exposure patterns (USEPA, 1980:iii). Since each state promulgates a different set of water quality standards and the majority of states have not made attempts to determine the adverse effects of chlorination or its by-products, there has been limited success in ensuring that public health and aquatic wildlife are adequately protected (USEPA, 1986:15).

2.5.1 Clean Water Act - Possible Reauthorization. The Environmental Protection Agency has proposed developing a plan for "reducing or prohibiting" the discharge of chlorine and chlorinated compounds into bodies of water as part of their recommendations on revising the Clean Water Act. The plan would call for the organization of a task force to study the human health effects and wildlife impact of chlorine and chlorinated compounds. The task force would be formed within six months of passing the revised Clean Water bill which is currently under consideration in the Senate (Noah, 1994). Environmentalist groups, such as Greenpeace's Toxics Campaign, lauded the EPA's proposal (Cushman, 1994). Also under consideration by the USEPA is a revision of the interim THM maximum contaminant level (MCL) for drinking water. They are proposing lowering the MCL from 100 ug/L to 50 or 25 ug/L based on the availability of technology to measure lower levels. The goal of the USEPA is to have an MCL of zero for THMs due to their potential carcinogenicity (Gilbert, 1992:140).

2.5.2 Public Concern. Many groups are calling for a ban on chlorine to eliminate the potential hazards of handling gaseous chlorine on public transportation systems, and

also to alleviate concerns about the toxicity of chlorine residual and chlorinated by-products. Greenpeace has focused their efforts on the health concerns of chlorine by-products in treated wastewater which end up in the food chain through fish and other animals (Noah, 1994). Greenpeace is calling for the elimination of chlorine from all industrial processes. This is an unprecedented effort in the history of environmentalism. The anti-chlorine campaign has already had some major successes: Europe's pulp and paper industry has eliminated the use of chlorine gas as bleach; the International Joint Commission on the Great Lakes has recommended broad chlorine phase-outs; and Norway has commissioned the Massachusetts Institute of Technology to study the policy implications of a total chlorine ban (Amato, 1993:152).

Based on the EPA's recommendations for the next CWA and on the public movement to minimize the damaging effects of chlorine; government agencies should be developing strategies to address this problem. The USAF discharges chlorinated effluent from fifteen of our wastewater treatment plants. It is our responsibility to ensure that our wastewater discharge does not contain enough THMs to damage the ecosystems of those bodies of water to which we discharge. Thus, in this study, I propose that a model can be used to predict the potential of a wastewater to form THMs and allow environmental managers to assess the ecological risk on the receiving body of water.

3.0 Methodology

3.1 Introduction

The use of natural system dynamics to assess the hazard of anthropogenic processes can be achieved by combining the efficiency and effectiveness of computer modeling with the comprehensive study of natural community dynamics. Estimating the ecological risk caused by THMs involves the incorporation of numerous parameters into a model to assess the overall THM formation potential of the effluent, and combining that assessment with ecotoxicological effect indices to estimate risk to the ecosystem. Modeling the THM formation potential allows environmental managers to quantify a risk based on the amount of THMs formed and comparing the amount to past research of the toxicity of THMs.

3.1.1 Research Process. The main objective of this research is to provide environmental managers with guidance on the THM formation potential of their WWTPs. Due to the extensive funding necessary to test for THMs and to perform a toxicological study of effluents, it was decided that modeling the formation of THMs and comparing the levels of THMs formed with past toxicity research would provide useful guidance to environmental managers.

To reach this objective, a model is needed to predict formation potential of AF WWTPs. To develop a model based on measured values, extensive data collection is needed. A linear regression is then performed using all variables involved in the formation of regulated THMs. The data needed to generate such a model includes the amount of precursors in the water, the temperature, the pH, the chlorine dose applied

to the water, the concentration of bromide in the water, the contact time of the chlorine, and the amount of THMs formed. Initial surveys were sent to all bases which currently operate a WWTP in conjunction with research being performed by Capt. Dave Piech. Follow-up surveys were sent to bases which use chlorine as a disinfectant. Copies of both are included in Appendix A. The objective of the surveys was to collect data to use in either constructing a model or to compare existing models. Of all the surveys sent out, only nineteen were returned and none contained data on the amount of THMs formed at the plant. The reason for the lack of data collected is funding. Since WWTPs are not required to monitor for THMs, the plants would need to contract for testing to be performed at their own expense.

An ongoing effort of the literature search was to ensure that a model had not already been developed to calculate the formation of THMs from chlorinating wastewater. To date, no THM formation potential model has been developed from wastewater data. Models have been developed for the formation of THMs using raw water data and making predictions based on drinking water treatment plant processes. No research has been done to validate the use of a drinking water treatment plant THM formation potential model using wastewater data. Therefore, an existing model and data was needed to assess WWTP THM formation potential. My research then focused on choosing a model, finding secondary data, calculating THM levels, and comparing those levels to ecotoxicological effect indices for the THMs. The models considered are discussed in section 3.2 and the toxicity levels used for comparison were taken from literature reviewed in section 2.4.

3.2 Available THM Formation Models.

Due to the interim THM maximum contaminant level (MCL) for drinking water of 100 ug/L, many models have been developed to predict the THM formation potential of a raw drinking water source. As previously stated, no models have been developed to predict the THM formation potential of wastewater effluent. The models currently being used by the drinking water community will be assessed for applicability with wastewater effluent.

The USEPA currently distributes a computer program which will predict the formation potential of THMs in drinking water disinfection systems. The Water Treatment Plant (WTP) program was originally developed to help drinking water plants assess the amount of DBPs they were producing to ensure compliance with the Disinfectant/Disinfection By-Products Rule promulgated in 1972. The program was prepared by the EPA for public distribution with the intention that the model predictions would be valid for average drinking water treatment plants. The program was not intended to predict exact treatment effects or water quality for each unique municipality (USEPA, 1994,1). The Windows 3.1© version is a user friendly computer program meant for use at treatment plants.

The WTP program has many unit processes which follow the treatment plan of a typical drinking water treatment plant. The program first estimates the amount of organic material removed by each individual process at the plant. Secondly, the program analyzes the fate and transport of the applied disinfectant as it passes through the drinking water treatment train. It then predicts concentrations of the disinfectant at the beginning and end of the train. The last step of the program predicts DBP

formation based on water quality and on the disinfectant concentration (USEPA, 1994a:A-1).

The last step in the WTP program, the prediction of DBPs, is the area of emphasis this research focuses on. The DBP formation sub-program is based on a model equation formulated in 1987 by Amy, Chadick, and Chowdhury. The EPA considered using three other THM formation models. The four models that the EPA considered are the most comprehensive models available to date to determine the DBP formation potential of a water. The same four models are considered for use with this research.

3.2.1 Christ and Deitz's Model. The first model considered was developed in 1988 by Christ and Deitz. It was based on the chlorination studies of two water sources in Florida. The model is dependent on TOC (mg/L), pH, time (t, hours), temperature (T, °Centigrade), chlorine dose (Cl₂, mg/L), and bromide concentration (Br, mg/L). It predicts THM formation in ug/L and is written as follows (USEPA, 1994a:A-2,3):

$$THM = 0.068(TOC)^{0.910}(pH)^{1.45}(T)^{0.652}(Cl_2)^{0.439}(Br)^{0.169}(t)^{0.240}$$

This model is based on data obtained from two similar water sources, therefore, it will probably not be as universally applicable as models based on many dissimilar water sources. Although it is not based on the largest database, its applicability for this research was considered.

3.2.2 Amy, Chadick, and Chowdhury's Model. Amy, Chadick and Chowdhury's research is based on 1090 data points collected from nine natural waters

from various locations in the continental US. The researchers first analyzed specific portions of the data base to determine which parameters effected THM formation. They then formulated two models: linear and non-linear multiple regression models. The researcher's goals were to develop a set of chemically rational and statistically valid models (Amy, 1987:89). Model formulas are given below:

Log-Log Model

$$\begin{aligned} \text{Total THM Formation Potential} = & 0.00309(\text{UV Absorbance} * \text{Total Organic Carbon})^{0.440} \times \\ & (\text{Chlorine Dose})^{0.409} \times (\text{Reaction Time})^{0.263} \times (\text{Temperature})^{1.06} \times (\text{pH} - 2.6)^{0.715} \\ & \times (\text{Bromide Concentration} + 1)^{0.0358} \end{aligned}$$

Non-Linear Model

$$\begin{aligned} \text{Total THM Formation Potential} = & -2.46 + 0.315(\text{UV Absorbance} * \text{Total Organic Carbon}) + \\ & 0.184\exp^{0.0762(\text{Temperature})} + 0.00611(\text{Chlorine Dose})^{1.33} + 0.215(\text{Bromide Concentration}) + 1.16(\text{Reaction} \\ & \text{Time})^{0.252} + 0.0887(\text{pH} - 2.6) \end{aligned}$$

The two models predict total THM formation potential based on numerous water quality characteristics. These characteristics will be outlined further in section 3.3. The two models developed by Amy *et al* were tested for applicability for this research because they are based on the widest range of water data to date and incorporate all pertinent variables of THM formation.

3.2.3 Engerholm's Model. The next DBP model considered for use was developed by Engerholm and Amy in 1983. It simulates the rate of chloroform formation in ug/L from the chlorination of a peat soil humic acid extract. The model incorporates the effects of pH, temperature, time (t, hours), TOC (mg/L), and the ratio of chlorine dose (mg/L) to TOC in the following formula (USEPA, 1994a:A-2,3):

$$CHCl_3 = k_1 k_2 (TOC)^{0.95} (Cl_2/TOC)^{0.28} (t)^z$$

The value of k_1 is pH dependent while the values of z and k_2 are temperature dependent. This model was not chosen for analysis because it is based on the formation of chloroform from a soil extract allowing limited applicability to the kinetics of THM formation in a WWTP.

3.2.4 Batchelor's Model. The third model considered was developed by Batchelor for the USEPA in 1989 based on results observed from Ohio River water from Cincinnati, Ohio. It simulates the formation and degradation of four THMs, five non-THM DBPs and total organic halogen (TOX). The model is based on a mechanistic approach instead of an empirical approach as the others are. The model is dependent on TOC, pH, time, bromide concentration and chlorine dose. Temperature was not considered due to lack of data. (USEPA, 1994a:A-2,3) This third model was not chosen because of the limited data source the model was based on (one source of test water) and the limited amount of research data available.

The three models chosen for comparison, Christ and Deitz's, Amy *et al's* log-log model and Amy *et al's* non-linear model, are analyzed for applicability with wastewater data. The model with the least mean squared error of predicted THM values versus measured THM values was chosen for use to determine THM formation potential of typical WWTP effluent.

3.2.5 The Use of Ecotoxicological Effect Indices. Calculated values from the chosen model will be compared with ecotoxicological effect indices given in section 2.4 to indicate risk to the receiving body of water and to human health if water re-use

is possible. These guidelines will be useful to environmental managers to assess overall ecosystem risk.

3.3 Development of the Models.

Amy *et al* used a series of experiments to study nine natural waters to determine the baseline conditions and ranges of parameters that their model could address. Their two models predict the THM formation potential (THMFP) of a natural water (Amy, 1987:89). Christ and Deitz's model predicts the THMFP of the two Floridian waters they based their research on (USEPA, 1994a:A-2,3). The THMFP of a water is an index of the potential extent of THM formation possible after the application of chlorine (Amy, 1987:89). It is a worst case estimate of THM formation. As defined by Amy *et al*, instantaneous THMs are THMs which are found already present in a water prior to a chlorination experiment (Amy, 1987:89). None of the waters Amy *et al* studied had instantaneous THMs and therefore their model values are equal to the terminal THMs (the addition of instantaneous THMs with THMFP) of the water (Amy, 1987:89).

Each water source used by Amy *et al* was measured for the following characteristics: THMFP measured using a standard liquid-liquid extraction test; non-purgeable organic carbon (NPOC) also identified as total organic carbon (TOC), measured using a total organic carbon analyzer; ultraviolet absorbance (UVABS), measured with a spectrophotometer (1-cm cell); color; relative fluorescence; ambient pH; ambient bromide concentration (BR), measured with an ion chromatograph; and turbidity, as well as others (Amy 1987:90). Values for the raw waters are given in Table 3.

Table 3 Raw Water Characteristics (Amy, 1987:90).

Water Source	NPOC	UVABS	pH	Bromide	THMFP*
Units	mg/L	cm ⁻¹		mg/L	ug/L
Edisto	11.30	0.489	7.30	0.074	1083
Scioto	6.25	0.152	7.60	0.098	336
Biscayne	6.50	0.251	7.30	0.151	296
Ilwaco	6.00	0.329	6.10	0.115	405
Kaw	5.22	0.153	7.70	0.152	267
Grasse	6.56	0.288	6.80	0.010	490
Pearl	5.62	0.136	6.60	0.051	303
James	13.80	0.296	8.00	0.254	694
Verde	3.00	0.063	8.30	0.111	97

*Standard THMFP test under the following conditions: 20°C, pH 7, a chlorine to NPOC ratio of 3.0 and a reaction time of 168 h.

THM formation related parameters such as TOC, TEMP, and UVABS, were analyzed for inclusion in Amy's models through the use of regressions. Each regression attempted to determine a correlation between THM formation potential and each parameter. Their results indicate that the multiplicative parameter TOC*UVABS was the best singular parameter to predict THM formation potential (Amy, 1987:91).

TOC is a means of defining the precursor concentration whereas UVABS is an indication of precursor reactivity. The UV absorbance of wastewater is quantified by a standard spectrophotometric absorbtion measurement at the key wavelength of 253.7 nm; this expresses the absorbtion (or transmittance) of energy per unit depth. The output is absorbance units/cm or a.u./cm (USEPA, 1986:159). This test would most likely give an indication of the presence of the carbonyl group in the compounds present in the water. The carbonyl group is responsible for the absorption of unsaturated ketones and aliphatic aldehydes (Calvert and Pitts, 1967:263). Examples of ketones and aldehydes which absorb in the 254 nm range are given in Table 4. The three models also incorporate the concentration of bromide in the input waters and

additional incremental effects on THM formation. This measurement is needed to determine the contribution of brominated haloforms to the total THM calculation.

Table 4 Ketones and Aldehydes Which Absorb at 254 nm
(Calvert and Pitts, 1967:368,369,377).

<u>Ketones</u>	<u>Aldehydes</u>
Acetone, CH ₃ COCH ₃ (220 to 320 nm)	Formaldehyde, CH ₂ O (240 to 360 nm)
Diethyl ketone, C ₂ H ₅ COC ₂ H ₅ (230 to 320 nm)	Propionaldehyde, C ₂ H ₅ CHO (230 to 340 nm)
	Acetaldehyde, CH ₃ CHO (230 to 340 nm)

Amy performed a series of kinetic experiments which varied pH, temperature (TEMP), chlorine dose (CLDOSE), reaction time (RXNTM), and bromide (BR) concentration from which a database of 1090 cases was compiled. A positive chlorine residual was maintained to ensure THM reactions occurred during the entire reaction time. The kinetic experiments varied parameters to the extent of the boundary condition given in Table 5 (Amy, 1987:92). Boundary conditions are not available for Christ and Deitz's model.

Table 5 Specified Boundary Conditions for Amy *et al* Model Parameters
(Amy, 1987:92).

Parameter	Boundary Conditions	Average Level
CLDOSE - mg/L	1.5 - 69	21.4
TEMP - °C	10 - 30	20
RXNTM - hours	0.1 - 168	
PH	4.6 - 9.8	7.3
BR - mg/L	0.010 - 1.245	0.112
TOC - mg/L	3.0 - 13.8	7.14
UVABS - cm ⁻¹	0.063 - 0.489	0.240
UVABS*TOC	0.189 - 5.53	1.98
Chlorine to TOC Ratio	0.5 - 5.0	3.0

The first of Amy *et al*'s models considered in this research is the recalibrated log-log model. Amy *et al* found that the formation of THMs under differing independent variables could be modeled by transforming both dependent and independent variables into natural log forms. Multiple linear regression was performed on the entire transformed database of 1090 cases. The value of $\ln(BR + 1)$ was used when it was realized that $\ln(BR)$ would produce negative values. The original version of the model produced a sum of the squares of the error (SSE) of 172 (Amy, 1987:92). The model was then recalibrated to include only those data points where a positive chlorine residual was maintained. The SSE dropped to 109 indicating a better fit for the predicted values (Amy, 1987:94). The recalibrated model is modified and expressed as a multiple parameter power function as follows:

$$\begin{aligned} \text{Total THM Formation Potential} = & 0.00309(\text{UV Absorbance} * \text{Total Organic Carbon})^{0.440} x \\ & (\text{Chlorine Dose})^{0.409} x (\text{Reaction Time})^{0.265} x (\text{Temperature})^{1.06} x (\text{pH} - 2.6)^{0.715} \\ & x (\text{Bromide Concentration} + 1)^{0.0358} \end{aligned}$$

Written Using Model Variables:

$$\begin{aligned} TTHM = & 0.00309(UVABS*TOC)^{0.440} x (CLDOSE)^{0.409} x (RXNTM)^{0.265} \\ & x (TEMP)^{1.06} x (PH-2.6)^{0.715} x (BR+1)^{0.0358} \end{aligned}$$

The model is applicable to the entire reaction time boundaries.

To develop Amy *et al*'s non-linear model, two sets of non-linear regressions were performed to represent long-term and short-term TTHM formation. The first set used data for a reaction time of 96 hours representative of long-term formation. The short-term non-linear regression used data with reaction times from 0.1 to 8 hours, 654

cases (Amy, 1987:92). The original version of the model was based on all 654 cases from the database, but some of the data was associated with a negative chlorine residual (cases where the chlorine to NPOC ratio was low). The researchers then recalibrated the model using only data where the chlorine residual remained positive. The SSE dropped from 229 for the original model to 219 for the recalibrated version. This recalibrated short-term model was considered for use in this research:

Short-term non-linear equation (RXNTM ≤ 8 h)

$$\begin{aligned} \text{Total THM Formation Potential} = & -2.46 + 0.315(\text{UV Absorbance} * \text{Total Organic Carbon}) + \\ & 0.184\exp^{0.0762(\text{Temperature})} + 0.00611(\text{Chlorine Dose})^{1.33} + 0.215(\text{Bromide Concentration})^{1.51} \\ & + 1.16(\text{Reaction Time})^{0.252} + 0.0887(\text{pH} - 2.6) \end{aligned}$$

Written Using Model Variables:

$$\begin{aligned} TTHM = & -2.46 + 0.315(\text{UVABS} * \text{TOC}) + 0.184\exp^{0.0762(\text{TEMP})} + 0.00611(\text{CLDOSE})^{1.33} \\ & + 0.215(\text{BR})^{1.51} + 1.16(\text{RXNTM})^{0.252} + 0.0887(\text{PH} - 2.6) \end{aligned}$$

A sensitivity analysis was performed on each model to determine a relative order of importance of the independent variables based on an incremental contribution to the model THM prediction. The log-log model analysis gave the following order of importance:

$$\text{TEMP} > \text{CLDOSE} > \text{PH} > \text{UVABS} * \text{TOC} > \text{RXNTM} > (\text{BR} + 1)$$

The non-linear model order of importance:

$$\text{RXNTM} > \text{TEMP} > \text{UVABS} * \text{TOC} > \text{PH} > \text{CLDOSE} > \text{BR}$$

The recalibrated log-log model provided the best overall fit of data (52 %) for the 1090 cases. Model performance varied from water to water, but the log-log format provided more accurate simulation than the non-linear simulation (Amy, 1987:96). Data on the performance of Christ and Deitz's model is unavailable.

3.4. Wastewater Characteristics.

Typical effluent characteristics are within the raw water boundary conditions of Amy *et al's* models. Effluent characteristic values are summarized in Table 6. The USEPA *Municipal Wastewater Disinfection Design Manual* gives typical UV absorbance values ranging from 0.087 to 0.175 cm^{-1} for tertiary treated effluent, 0.13 to 0.22 cm^{-1} for secondary treatment, and 0.174 to 0.35 cm^{-1} for primary treatment (USEPA, 1986:159). Total organic carbon measurements range from 80 to 290 mg/L before treatment (Tchobanoglous, 1991:109). With the removal efficiency of WWTPs approximately 90% for secondary treatment, a final effluent could have TOC values in the range of 8 to 29 mg/L (Tchobanoglous, 1991:548). The use of TOC by Amy *et al's* model is actually a measure of DOC (dissolved organic carbon) by operational definition (USEPA, 1994a:A-2). Values for pH usually range from 6.5 to 9.0 based on state mandated permitting. Depending on the geographic location of the plant, temperatures range from 10 to 21.1 ° C with 15.6 ° C as a representative value (Tchobanoglous, 1991:62). These values are expected to give reasonable predictions of

THMFP since Amy *et al's* models were most accurate when temperature and pH levels were at ambient conditions (temp = 20°C and pH = 7.3) and less accurate at high and low extremes.

Table 6 Typical WWTP Effluent Characteristics

<u>Characteristic</u>	<u>Range</u>
UVABS Primary Effluent	0.174 to 0.35 cm ⁻¹
UVABS Secondary Effluent	0.13 to 0.22 cm ⁻¹
UVABS Tertiary Effluent	0.087 to 0.175 cm ⁻¹
TOC	8 to 29 mg/L
pH	6.5 to 9.0
Temperature	10 to 21.1 ° C

3.4.1 Chlorination Process. Amy *et al's* models were most accurate in simulating results obtained from THMFP experiments that employed high chlorine to NPOC ratios (3.0 to 5.0) (mass basis) (Amy, 1987:91). The practice of "breakpoint" chlorination at a typical WWTP would create lesser chlorine to NPOC ratios (1.75 and less) (Singer data, 1988). The models predictions will be compared to measured values to show validity at these lesser chlorine to NPOC ratios. Typical chlorination contact chambers retain wastewater for a contact time of 30 minutes. The contact time is usually specified by regulatory agencies and ranges from 15 minutes at maximum design flow to 45 minutes (Tchbanoglous, 1991:501). Reaction time boundaries are not available for Christ and Deitz's model and Amy *et al's* models are valid at contact times less than 8 hours for the non-linear model and for any time between 0.1 to 168 hours for

the log-log model. Based on the above valid contact times, typical WWTP chlorination contact times will be assumed valid for use.

3.5 Effluent Data

Due to a lack of relevant data from Air Force WWTPs, a source for data was needed. Two research efforts were found that had past or ongoing efforts to analyze THM formation from the chlorination of wastewater. Both efforts were well documented and reliable sources of THM analyses.

3.5.1 Sources of Data. A study was conducted in 1988 to examine the formation of disinfection by-products resulting from the chlorination of municipal wastewater from three plants located in North Carolina. The research was sponsored by a grant from the Water Resources Research Institute of the University of North Carolina and performed by Philip C. Singer, Richard A. Brown, and Joseph F. Wiseman, Jr. of the Department of Environmental Sciences and Engineering. One of their overall research objectives was to quantify the formation of THMs and total organic halides (TOX) resulting from chlorination of treated effluent (Singer, 1988:3). The investigation involved both laboratory and field experiments. The field experiments were conducted at Orange Water and Sewer Authority (OWASA)-Mason Farm WWTP, Durham-Northside WWTP and Greensboro - North Buffalo Creek WWTP. Each of the three plants employed trickling filters followed by activated sludge and chlorine disinfection (Singer, 1988:25). Since the plants were similar in process to the majority of AF WWTPs, their data was chosen to be used for model calculations. During four of the five field sampling trips, "breakpoint" chlorination was occurring. The chlorine to

ammonia molar ratio was above 2.0 (Singer, 1988:57). This indicates typical chlorination practices. The OWASA chlorine contact chamber provided for a contact time of 1 hour at a design flow rate of 8 MGD (Singer, 1988:25). At the Durham-Northside WWTP, chlorination occurs by injecting a concentrated liquid chlorine into the head of the discharge pipe. Mixing and contact occur in the underground pipe which discharges to a drainage ditch. The stated contact time for the pipe and drainage ditch, before discharge to Ellerbee Creek, is 15 minutes (Singer, 1988:37). Effluent from the Greensboro North Buffalo Creek WWTP was not monitored for DBP formation.

THM analyses samples were taken at the two plants before chlorination and at points within and following the chlorination contact systems. Samples were collected to minimize loss of VOCs. Sodium sulfite was added to quench any residual chlorine remaining in the samples (Singer, 1988:46). The four regulated THMs were detected using liquid-liquid extraction, with gas-chromatograph analysis. The detection limit for the THMs was estimated at 1 ug/L (Singer, 1988:50).

A set of controlled laboratory experiments was also conducted by Singer *et al.* OWASA effluent was collected prior to disinfection and experiments were conducted within 12 - 24 hours. Samples were analyzed for TOC, temperatures and pH were measured and chlorine was injected into the sample while being uniformly mixed. Varying contact times were used to measure TOX and THM formation (Singer, 1988:97). Complete details of both field and laboratory experiments are given in Singer *et al.* The data collected from twelve of their experiments is given in Table 7.

Another source of data was research performed by Joan A. Oppenheimer and John E. Hoagland. The objectives of their study were to investigate required doses of chlorine versus ultraviolet light required to inactivate a target list of pathogens and to identify any DBPs formed and the toxicity of the effluents. Experiments were

performed on bench-scale efforts to control conditions. The experiments used tertiary effluent from the Elsinore Valley Municipal Water District Regional plant 80 miles southeast of Los Angeles. Volatile organic compound analysis of the tertiary effluent was performed preceding and following disinfection. Bench scale experiments used a chlorine batch reactor for a two hour contact time. Chlorine dose was varied to mimic full-scale requirements (Oppenheimer, 1993:15). DBP analysis of the bench scale test, performed using full-scale plant conditions for chlorine dose and contact time, indicated the formation of THMs as well as other DBPs (Oppenheimer, 1993:23). During this experiment, the UV absorbance of the effluent was also recorded. Data from this study is given in Table 7.

Table 7. Secondary Data (Singer, 1988 and Oppenheimer, 1993).

<u>Date</u>	<u>TOC</u>	<u>CLDOSE</u>	<u>TEMP</u>	<u>RXNTM</u>	<u>PH</u>	<u>UVABS</u>	<u>THM</u>
	mg/L	mg/L	°C	hr		cm ⁻¹	ug/L

Field Studies Data OWASA-Mason Farm WWTP

13 Nov 83	8.0	2.3	20	1	7.2	-	4.0
6 Jan 84	7.5	2.4	10	1	6.9	-	6.0

Field Studies Data Durham-Northside WWTP

11 Jan 84	27.5	6.2	12	.25	7.0	-	39.0
15 Jan 85	27.5	2.0	14	.25	7.1	-	28.0
16 Jan 85	27.5	2.0	14	.25	7.2	-	57.0

Laboratory Studies Data OWASA-Mason Farm WWTP

20 Feb 85	7.4	10.2	24	2.0	6.9	-	71.0
20 Feb 85	7.4	10.2	24	1.0	6.9	-	60.0
20 Feb 85	7.4	10.2	24	050	6.9	-	48.0
20 Feb 85	7.4	10.2	24	025	6.9	-	41.0
20 Feb 85	7.4	2.55	24	1.0	6.9	-	12.0
1 Mar 85	6.6	10.2	26	1.0	6.9	-	67.0

Laboratory Studies Data Elsinore Valley Municipal Water District WWTP

19 Jan 93	5.6	9.82	22	2.0	7.7	.132	47.1
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- Indicates value not measured

3.5.2 Assumptions for Model Use. The first assumption that had to be made to consider the Singer and Oppenheimer data valid for use with the three models, was the assumption that all measurements given, where processes were not documented, were performed according to valid testing standards. The next assumption made was that the three TOC measurements which were higher than the specified boundary conditions of Amy *et al's* models would not invalidate the models due to TOC's lower precedence in contributing to THM formation. Bromide concentrations were not measured for any of the secondary data points, therefore, all calculations will include a bromide concentration of 0.01 mg/L, the minimum boundary condition for Amy *et al's* models. Since the bromide concentration has the least effect on THM prediction, this assumption should have minimal effect on model predictive capability. The last assumption which was initially made, was that the dependent variable, UVABS, could be either calculated using Amy *et al's* model, correlated to TOC based on the UVABS and TOC of the Oppenheimer experiment, or specified at a median value for secondary effluents without affecting the overall predictive capability of the models. This assumption was necessary since the Singer experiment did not measure UVABS. This assumption was tested and is presented in Section 4.2.

4.0 Results and Discussion

4.1 Introduction

Two calculation steps were needed prior to comparison of the three models. First, an actual calculation of the models using the author's verification data was needed to ensure that the models were being used correctly. Since the documentation found on Christ and Deitz's model did not provide verification data, this step could only be verified for Amy *et al's* models. The second set of calculations were needed to provide the missing values for UVABS.

4.2 Verification of Calculations

The first step towards verification was to compare Amy *et al's* validation data with calculated values using the model. The first set of data validated was Amy *et al's* data from Morgan Creek, North Carolina. Using the recalibrated log-log model, Amy *et al's* predicted total THM calculation of 2.02 $\mu\text{mol/L}$ is verified. The verified value of 2.15 is only 0.13 $\mu\text{mol/L}$ larger than Amy *et al's* THM calculation. The second set of data validated was a calculation of 1.13 $\mu\text{mol/L}$ from Glenmore Reservoir, New

York. The verified calculation of 1.12 is only 0.01 umol/L smaller than Amy *et al's* calculated THM value. These data calculations are summarized in Table 8.

The validation of my computation of Amy *et al's* recalibrated non-linear model follows in the same manner using more of Amy's validation data. Amy's calculation of

Table 8 Verification of Log-Log Model Calculations

<u>UVABS*TOC</u>	<u>CLDOSE</u>	<u>TEMP</u>	<u>RXNTM</u>	<u>BR</u>	<u>PH</u>	<u>Verified Calculation</u>	<u>Original Calculation</u>
mg/cm*L	mg/L	°C	hours	mg/L		umol/L	umol/L
3.66	20	23	4	0	7.0	2.15	2.02
0.968	20	20	4	0	7.5	1.12	1.13

0.250 umol/L THM for Holston River is 0.02 umol/L less than my calculation. The calculation of 1.31 umol/L for Grasse River is 0.02 larger than my calculation. The non-linear model data points are given in Table 9. Based on these four calculations, my computations of Amy's log-log and non-linear models are validated.

Table 9 Verification of Non-Linear Model Calculations

<u>UVABS*TOC</u>	<u>CLDOSE</u>	<u>TEMP</u>	<u>RXNTM</u>	<u>BR</u>	<u>PH</u>	<u>Verified Calculation</u>	<u>Original Calculation</u>
mg/cm*L	mg/L	°C	hours	mg/L		umol/L	umol/L
0.531	10	20	1	0.04	7.4	0.27	0.25
2.45	20	20	2	0.01	7.4	1.29	1.31

Given that the calculation of Amy *et al's* two models is being performed correctly, the next step towards using the models to predict THM formation potential (THMFP) is to understand the influence of UVABS and TOC on the models. Using the Singer wastewater characteristics and the measured THM values, the log-log model is used to solve for a characteristic UVABS value of the Singer wastewater data.

4.3 Calculation of UVABS Value for Singer Data.

Two different methods are employed to define UVABS values for the Singer data. The two sets of UVABS values will be used in both of Amy *et al*'s models to compare influence of UVABS on the predictive capability of the models.

4.3.1 Solving for UVABS. The recalibrated log-log model is used to solve for a characteristic value of UVABS using two different reaction times for the same wastewater. It is shown on the next page that the calculated value for UVABS is 0.07 using Singer data.

UVABS Calculation for OWASA Wastewater (Singer, 1988: 115)

TEMP in degrees Celcius	TOC in mg/L	CLDOSE in mg/L
TEMP := 24	TOC := 7.4	CLDOSE := 10.2
PH := 6.9	RXNTM in hours	BR is bromide content in mg/L
	RXNTM := 1	BR := 0.0

To convert to ugrams/L. to allow for comparison I assume no contribution from bromide and convert for an average molecular weight of 119 for chloroform:

AMW := 119 grams/mol THMFP := 60 ugrams/L given TTHM := $\frac{\text{THMFP}}{\text{AMW}}$

TTHM = 0.5042 TTHM in umoles/L

Using the recalibrated log-log model:

$$\text{LNUV} := \frac{\ln \left[\frac{\text{TTHM}}{(\text{BR} + 1)^{0.0358} \cdot (\text{PH} - 2.6)^{0.715} \cdot \text{TEMP}^{1.06} \cdot \text{RXNTM}^{0.265} \cdot \text{CLDOSE}^{0.409} \cdot 0.00309} \right]}{0.440} - \ln(\text{TOC})$$

LNUV = -2.6076 UVABS := exp (LNUV) UVABS = 0.0737

Verification calculation:

TEMP in degrees Celcius	TOC in mg/L	CLDOSE in mg/L
TEMP := 24	TOC := 7.4	CLDOSE := 10.2
PH := 6.9	RXNTM in hours	BR is bromide content in mg/L
	RXNTM := 2	BR := 0.0

To convert to ugrams/L. to allow for comparison I assume no contribution from Bromine and convert for an average molecular weight of 119 for chloroform:

AMW := 119 grams/mol
THMFP := 71 ugrams/L

TTHM := $\frac{\text{THMFP}}{\text{AMW}}$ TTHM = 0.5966 TTHM is given in umoles/L

Using the recalibrated log-log model:

$$\text{LNUV} := \frac{\ln \left[\frac{\text{TTHM}}{(\text{BR} + 1)^{0.0358} \cdot (\text{PH} - 2.6)^{0.715} \cdot \text{TEMP}^{1.06} \cdot \text{RXNTM}^{0.265} \cdot \text{CLDOSE}^{0.409} \cdot 0.00309} \right]}{0.440} - \ln(\text{TOC})$$

LNUV = -2.6425 UVABS := exp (LNUV) UVABS = 0.0712

Based on USEPA's Disinfection Manual, the UVABS range for effluent is from 0.087 to 0.35 cm⁻¹, therefore, the calculated UVABS is at the lower end of standard measurements. To compare the influence of UVABS on Amy *et al*'s models, a value comparable to Oppenheimer's measured UVABS of 0.132 cm⁻¹ will also be used.

These two values for UVABS will be used in the log-log model and the non-linear model and the models' performance will be analyzed.

4.3.2 Correlating UVABS to TOC. Since Oppenheimer's research measured a value for UVABS, a multiplicative constant can be assumed to correlate TOC and UVABS. With TOC=5.6 and UVABS=0.132, the multiplier is equal to 0.02357.

$$UVABS = 0.02357(TOC)$$

It is assumed that if Singer's TOC values are multiplied by this constant, UVABS values will be correlated to the TOC values in a logical manner. Correlated values are given in Table 10.

Table 10 Correlated UVABS Values

TOC mg/L	UVABS 1/cm
8.0	0.188
7.5	0.177
27.5	0.648
7.4	0.174
6.6	0.155
5.6	0.132

These values for will also be used in the log-log model and the non-linear model and the models' performance will be analyzed.

4.4 Comparison of Models.

Using the three values of UVABS, 0.07 cm^{-1} , 0.13 cm^{-1} , and the correlated values, EXCEL is used to calculate the THMFP values using all three models. Data points used are the data from Singer and Oppenheimer as given in Table 7 except for the inclusion of the three different UVABS values for Singer's data. The calculations are given in Tables 11 through 14.

**Table 11. Calculations of Log-Log and Non-Linear Model Predictions
With UVABS Equal to 0.07 cm^{-1} .**

<u>TOC</u> mg/L	<u>CLDOSE</u> mg/l	<u>UVABS</u> cm^{-1}	<u>TEMP</u>	<u>RXNTM</u> hr	<u>BR</u> mg/L	<u>PH</u>	<u>Log-Log</u> <u>THMFP</u> ug/L	<u>Non-Linear</u> <u>THMFP</u> ug/L
8.0	2.3	0.070	20	1.00	0.01	7.2	32.17	19.81
7.5	2.4	0.070	10	1.00	0.01	6.9	14.54	-45.47
27.5	6.2	0.070	12	0.25	0.01	7.0	32.44	-15.67
27.5	2.0	0.070	14	0.25	0.01	7.1	24.44	-11.56
27.5	2.0	0.070	14	0.25	0.01	7.2	24.83	-10.37
7.4	10.2	0.070	24	2.00	0.01	6.9	79.42	100
7.4	10.2	0.070	24	1.00	0.01	6.9	66.10	70.32
7.4	10.2	0.070	24	0.50	0.01	6.9	55.01	45.4
7.4	10.2	0.070	24	0.25	0.01	6.9	45.78	24.47
7.4	2.6	0.070	24	1.00	0.01	6.9	37.49	55.19
6.6	10.2	0.070	26	1.00	0.01	6.9	68.42	93.24
5.6	9.8	0.132	22	2.00	0.01	7.7	89.82	92.85

**Table 12. Calculations of Log-Log and Non-Linear Model Predictions
With UVABS Equal to 0.13 cm⁻¹.**

<u>TOC</u> mg/L	<u>CLDOSE</u> mg/l	<u>UVABS</u> cm ⁻¹	<u>TEMP</u>	<u>RXNTM</u> hr	<u>BR</u> mg/L	<u>PH</u>	<u>Log-Log</u> <u>THMFP</u> ug/L	<u>Non-Linear</u> <u>THMFP</u> ug/L
8.0	2.3	0.13	20	1.00	0.01	7.2	39.98	37.93
7.5	2.4	0.13	10	1.00	0.01	6.9	18.07	-25.05
27.5	6.2	0.13	12	0.25	0.01	7.0	40.31	51.11
27.5	2.0	0.13	14	0.25	0.01	7.1	30.37	55.0
27.5	2.0	0.13	14	0.25	0.01	7.2	30.85	56.13
7.4	10.2	0.13	24	2.00	0.01	6.9	98.70	112.38
7.4	10.2	0.13	24	1.00	0.01	6.9	82.14	84.30
7.4	10.2	0.13	24	0.50	0.01	6.9	68.35	60.71
7.4	10.2	0.13	24	0.25	0.01	6.9	56.88	40.90
7.4	2.6	0.13	24	1.00	0.01	6.9	46.59	69.97
6.6	10.2	0.13	26	1.00	0.01	6.9	85.02	104.07
5.6	9.8	0.132	22	2.00	0.01	7.7	89.82	92.85

**Table 13. Calculations of Log-Log and Non-Linear Model Predictions
With Correlated UVABS Values.**

<u>TOC</u> mg/L	<u>CLDOSE</u> mg/l	<u>UVABS</u> cm ⁻¹	<u>TEMP</u>	<u>RXNTM</u> hr	<u>BR</u> mg/L	<u>PH</u>	<u>Log-Log</u> <u>THMFP</u> ug/L	<u>Non-Linear</u> <u>THMFP</u> ug/L
8.0	2.3	0.188	20	1.00	0.01	7.2	45.51	54.65
7.5	2.4	0.177	10	1.00	0.01	6.9	20.14	-10.67
27.5	6.2	0.648	12	0.25	0.01	7.0	70.85	537.76
27.5	2.0	0.648	14	0.25	0.01	7.1	53.37	541.13
27.5	2.0	0.648	14	0.25	0.01	7.2	54.22	542.10
7.4	10.2	0.174	24	2.00	0.01	6.9	109.33	122.18
7.4	10.2	0.174	24	1.00	0.01	6.9	90.99	94.82
7.4	10.2	0.174	24	0.50	0.01	6.9	75.72	71.83
7.4	10.2	0.174	24	0.25	0.01	6.9	63.01	52.53
7.4	2.6	0.174	24	1.00	0.01	6.9	51.61	80.86
6.6	10.2	0.155	26	1.00	0.01	6.9	90.44	108.94
5.6	9.8	0.132	22	2.00	0.01	7.7	89.82	92.85

Table 14. Calculations of Christ and Deitz's Model.

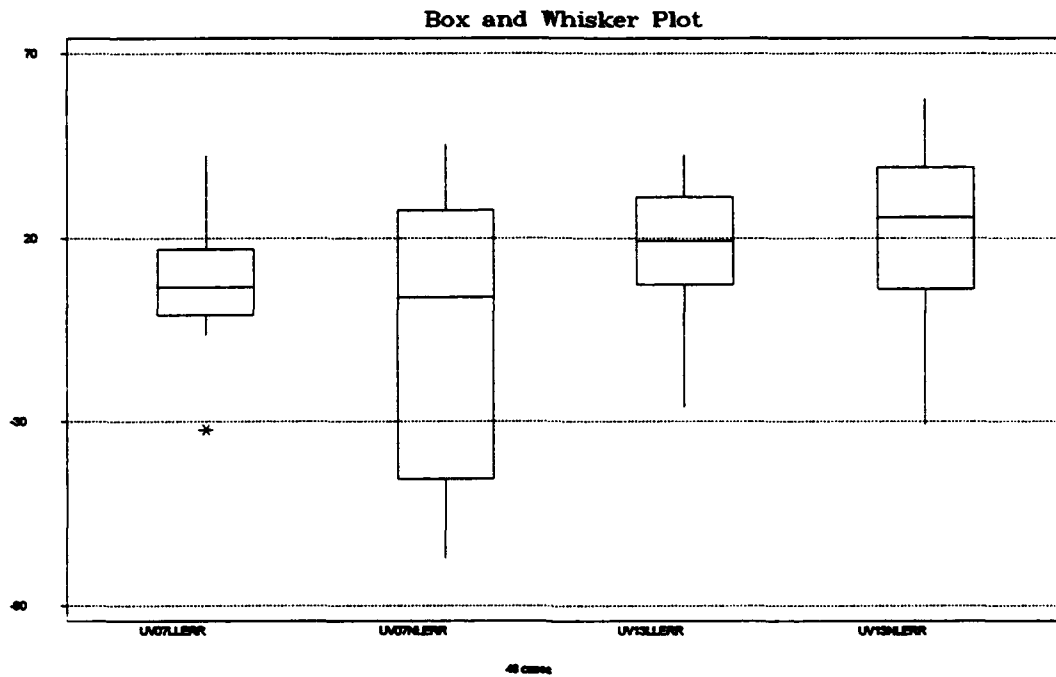
<u>TOC</u> mg/L	<u>CLDOSE</u> mg/l	<u>TEMP</u>	<u>RXNTM</u> hr	<u>BR</u> mg/L	<u>PH</u>	<u>THMFP</u> ug/L
8.0	2.3	20	1.00	0.01	7.2	36.86
7.5	2.4	10	1.00	0.01	6.9	21.19
27.5	6.2	12	0.25	0.01	7.0	86.43
27.5	2.0	14	0.25	0.01	7.1	59.37
27.5	2.0	14	0.25	0.01	7.2	60.59
7.4	10.2	24	2.00	0.01	6.9	82.56
7.4	10.2	24	1.00	0.01	6.9	69.91
7.4	10.2	24	0.50	0.01	6.9	59.19
7.4	10.2	24	0.25	0.01	6.9	50.12
7.4	2.6	24	1.00	0.01	6.9	38.04
6.6	10.2	26	1.00	0.01	6.9	66.37
5.6	9.8	22	2.00	0.01	7.7	70.14

Forecasting accuracy of a model is measured by looking at the sizes and signs of the residuals between actual measured values and model predictions. The residuals for all calculations are given in Table 15. The central tendency and variability of the residuals

Table 15 Error Values.

Measured Value	Log-Log Error	Non-Linear Error	Log-Log Error	Non-Linear Error	Log-Log Error	Non-Linear Error	Christ and Deitz Error
	UVABS = 0.07	UVABS = 0.07	UVABS = 0.13	UVABS = 0.13	Correlated UV	Correlated UV	
4.0	28.17	15.81	35.98	33.93	41.51	50.65	32.86
6.0	8.54	-51.47	12.07	-31.05	14.14	-16.67	15.19
39.0	-6.56	-54.67	1.31	12.11	31.85	498.76	47.43
28.0	-3.56	-39.56	2.37	27.00	25.37	513.13	31.37
57.0	-32.17	-67.37	-26.15	-0.87	-2.78	485.10	3.59
71.0	8.42	29.00	27.70	41.38	38.33	51.18	11.56
60.0	6.10	10.32	22.14	24.30	30.99	34.82	9.91
48.0	7.01	-2.60	20.35	12.71	27.72	23.83	11.19
41.0	4.78	-16.53	15.88	-0.10	22.01	11.53	9.12
12.0	25.49	43.19	34.59	57.97	39.61	68.86	26.04
67.0	1.42	26.24	18.02	37.07	23.44	41.94	-.063
47.1	42.72	45.75	42.72	45.75	42.72	45.75	23.04

**Figure 3 Plot of Error for Log-Log and Non-Linear Models
With UVABs Values of 0.07 and 0.13 cm⁻¹.**



or errors can be viewed using a box and whisker plot. The box encloses the middle half of the error values specified with a line bisecting the box at the median value. The vertical lines indicate the range of typical error values. Extreme values are displayed as “*” for possible outliers and as an “o” for probable outliers. Box and whisker plots of the errors between measured and forecasted values of the log-log model and the non-linear model for UVABS values of 0.07 cm⁻¹ and 0.13 cm⁻¹ are given in Figure 3. It is shown by the variances of the error values, that the non-linear model is less accurate at predicting THM formation than the log-log model regardless of the UVABS values. This is likely due to the original error in that form of the model.

Figure 4 Plot of Error for Log-Log and Non-Linear Models With Correlated UVABS Values and Christ and Deitz's Model.

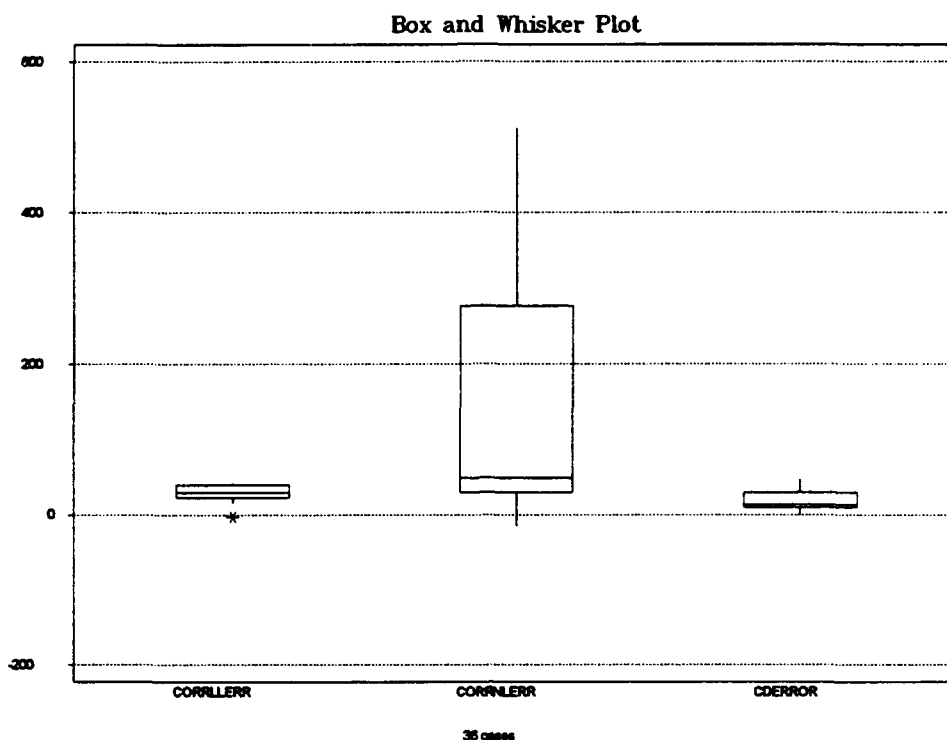


Figure 4 shows the errors for the log-log and non-linear models using correlated UVABS values and the error of Christ and Deitz's model. The variance of the prediction errors associated with the non-linear model is much larger than the log-log model and Christ and Deitz's model predictions. The error points which are on the high extreme on the non-linear model plot are caused because of the correlation of UVABS to high TOC values (27.5 mg/L). Amy *et al* recommend that values above 13.8 mg/L not be used in their model. It is easy to see here that the non-linear model cannot be used with UVABS values correlated to TOC values higher than the specified boundary conditions. It may be possible to correlate a typical UVABS of a water

source to its TOC measurement, but that correlation coefficient will not be that same for different water sources. Regardless of the UVABS value, the overall error is once again greater for the non-linear model than the log-log model.

Another way to compare error values, is to calculate the mean squared error (MSE) of the data sets. The MSE attempts to average the sizes of forecast errors by averaging the squares of the errors. Because the MSE uses squared error terms it gives more weight to large forecast errors and less to smaller forecast errors (Farnum, 1989: 24). A model which produces uniform small errors is preferred over a model which produced erratic large errors. A certain amount of MSE is inevitable for all models. The MSE is calculated by summing the forecast errors squared and dividing by the number of forecasts. Based on the given box and whisker plots, the four most accurate data sets are selected for MSE calculation. Those data sets are: Christ and Deitz's model, the log-log model with correlated UVABS data, and the log-log model with UVABS values set at 0.07 and 0.13 cm^{-1} . MSE calculations were performed using MathCAD and are shown on the following page.

The MSE for Christ and Deitz's predictions is calculated:

$$A := 32.86^2 + 15.19^2 + 47.43^2 + 31.37^2 + 3.59^2 + 11.56^2$$

$$\text{christMSE} = \frac{A + 9.91^2 + 11.19^2 + 9.12^2 + 26.04^2 + (-.63)^2 + 23.04^2}{12} \quad \text{christMSE} = 517.22$$

The MSE for the Log-Log model predictions with correlated UVABS values:

$$B := 41.51^2 + 14.14^2 + 31.85^2 + 25.37^2 + (-2.78)^2 + 38.33^2$$

$$\text{corrllMSE} = \frac{B + 30.99^2 + 27.72^2 + 22.01^2 + 39.61^2 + 23.44^2 + 42.72^2}{12} \quad \text{corrllMSE} = 934.55$$

The MSE for the Log-Log model predictions with UVABS = 0.07:

$$C := 28.17^2 + 8.54^2 + (-6.56)^2 + (-3.56)^2 + (-32.17)^2 + 8.42^2$$

$$\text{spec1llMSE} = \frac{C + 6.10^2 + 7.01^2 + 4.78^2 + 25.49^2 + 1.42^2 + 42.72^2}{12} \quad \text{spec1llMSE} = 384.496$$

The MSE for the Log-Log model predictions with UVABS = 0.13:

$$D := 35.98^2 + 12.07^2 + 1.31^2 + 2.37^2 + (-26.19)^2 + 27.70^2$$

$$\text{spec4llMSE} = \frac{D + 22.14^2 + 20.35^2 + 15.88^2 + 34.59^2 + 18.02^2 + 42.72^2}{12} \quad \text{spec4llMSE} = 616.78$$

It is shown that the MSE of the log-log model using correlated UVABS values (934.55) is almost three times as large as MSE of the log-log model with a UVABS set at 0.07 (384.50). The larger error of the correlated data is once again likely due to the correlation of UVABS to the three high TOC values. Although all four data sets have a very large MSE, indicating a poor fit of forecasted data, the log-log model using a

characteristic UVABS value or Christ and Deitz's model, when UVABS data is not available, would prove the best choices for use with WWTP data.

The THMFP predictions given in Tables 11 for the log-log model using a UVABS value of 0.07 cm^{-1} and in Table 14 for Christ and Deitz's model are graphed on scatter plots versus the measured values to show degree of error for both models (Figures 5 and 6). The line shown is a best fit of the plotted points, called the regression line for the plot. A perfect model would plot all points along a 45° line.

Figure 5 Scatter Plot of Data Predicted by Log-Log Model
Using UVABS = 0.07 cm^{-1} .

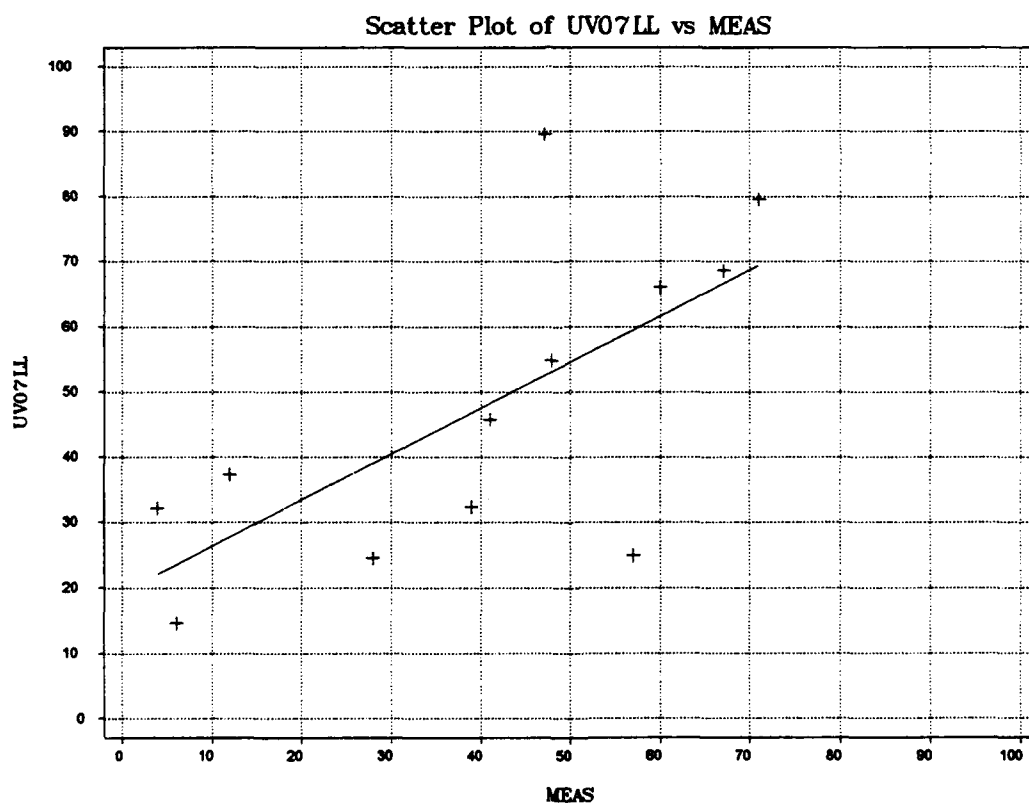
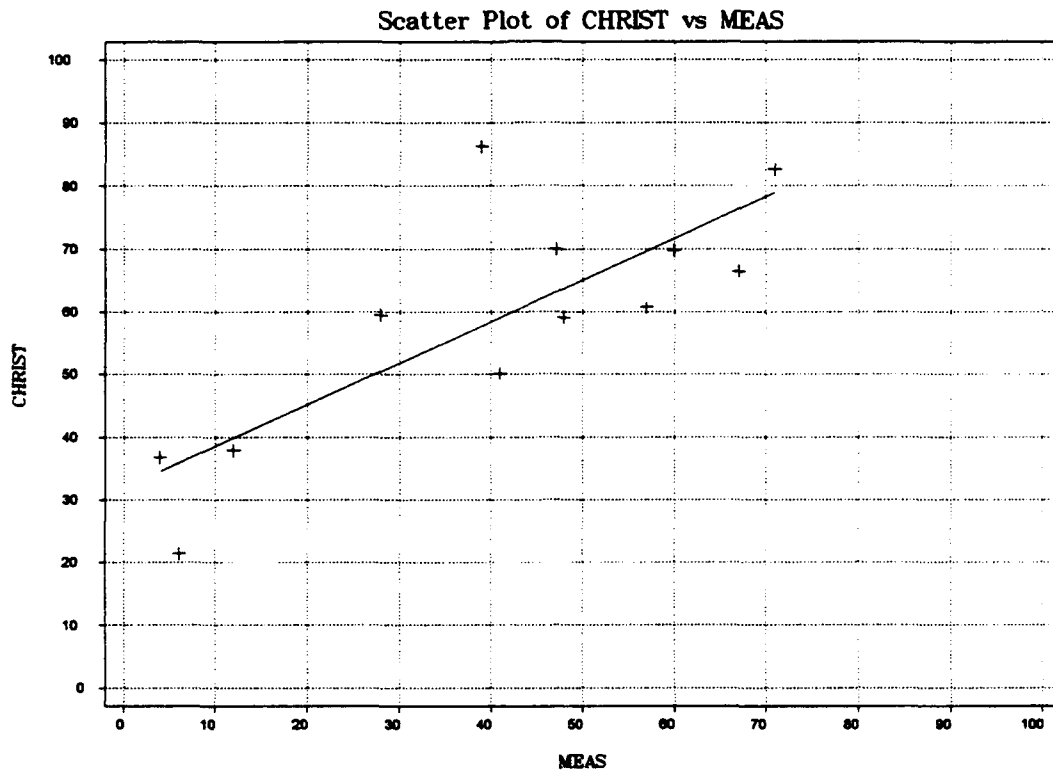


Figure 6 Scatter Plot of Data Predicted by Christ and Deitz Model



Both scatter plots indicate a large degree of error, however, the log-log model provided better overall predictive capability than Christ and Deitz's.

4.5 Modeling Results Using Typical WWTP Data.

The predictive abilities of Amy *et al's* model for use with wastewater is dependent upon the wastewater effluent fitting within the set boundaries of the model. The typical ranges of WWTP data described in section 3.4 are used as input to Amy *et*

al's recalibrated log-log model to provide predictions for THMFP of WWTPs. Values of TOC higher than the model boundary of 13.8 mg/L, and the chosen UVABS value of 0.070 cm-1 are used understanding that TOC and UVABS have less influence on the model's predictive capability than do temperature, chlorine dose, and pH.

4.5.1 Influence of Chlorine Dose, Contact Time, Temperature and pH. These four measurements were varied over a range of TOC values from 5 to 30 mg/L simulating the ranges of measurements that typical WWTPs may encounter. THMFP values were calculated using Amy *et al's recalibrated log-log model*. Simulations are given in Appendix B. Model predictions are considered worse case predictions based on the predicted versus measured error calculations performed in section 4.4. The simulations showed that THMFP values become higher than the drinking water standard of 100 ug/L only when TOC values approach the high end of typical WWTP operating values and a high chlorine dosage is administered.

A longer reaction time dramatically effects the amount of THMFP predicted. Using a median temperature of 20 degrees, a mid-range chlorine dose of 10 mg/L, and a pH of 7, an increase in reaction time from .25 hour to 1 hour caused the THMFP to rise from 70.44 ug/L to 101.70 ug/L at a TOC of 30 mg/L. At low flow conditions, the reaction time of a typical WWTP may be delayed to as long as 1 hour causing high levels of DBPs to be formed.

Changes in temperature also have dramatic effects on the amount of THMFP predicted. A rise in fifteen degrees, holding all other variables constant, will rise the THMFP prediction from 40.60 ug/L to 107.22 ug/L for a TOC value of 30 mg/L. PH values do not have as much of an influence on the THMFP values. As the pH is changed from 6.0 to 9.0, predictions only rise 40.25 ug/L.

4.5.2 Influence of Precursor Organics in Wastewater. The rise in THMFP is evident as TOC values increase. With very low TOC levels, the model predicts quantities which are well below the drinking water standard. Only when the TOC values rise above 24 mg/L do THMFP predictions reach 100 ug/L.

4.6 Discussion of Results

Environmental managers may assess the THMFP of their WWTP by using the simulations in Appendix B. The values given are worst case predictions of THMFP based on typical plant and effluent characteristics. If the means to measure the necessary data points is available, managers can calculate the THMFP of their WWTP using Amy *et al's* model.

The ambient water quality criteria for the halomethanes is in the range of 1,000 ug/L for aquatic species embryo stages to 30,000 ug/L for acute toxicity of adults.

Since the US Safe Drinking Water THM standard has been set at 100 ug/L, comparisons to this lower standard are made.

Based on the typical wastewater THMFP calculation varying TOC, it can be seen that values of THMFP only approach the 100 ug/L standard when TOC values rise higher than 24 mg/L combined with other variables at the high ends of their ranges. Knowing that a TOC value of 30 mg/L is the high end of the range for a primary treatment plant, AF WWTPs values will typically be lower. Thirteen of the fifteen plants which release chlorinated effluent have secondary or tertiary treatment trains, bringing the average TOC value well below 30 mg/L. The minimal amount of THMs predicted will volatilize quickly if the body of water is aerated at all. This process further minimizes the risk to down stream human health.

5.0 Conclusions and Recommendations

Chlorine disinfection is used extensively by Air Force WWTPs. Despite its effectiveness as a biocide, the use of chlorine as a disinfectant may cause the formation of THMs which can have detrimental effects on the bodies of water to which we discharge and to human health. The concern over the formation of THMs in drinking water treatment plants has led to drinking water standards and the development of many models. Concerns over the DBPs formed through wastewater chlorination have led to investigations of the potential toxicity of wastewaters and is leading government agencies to re-evaluate requirements for wastewater disinfection practices.

This research was conducted to ensure that Air Force environmental managers are aware that our WWTPs may be producing DBPs. Guidance given in Appendix B may be used to find a worst case prediction of a plant's THMFP. If data points are available, Amy *et al's* model may be used to calculate the same prediction more accurately. Results indicate that THMFP is typically lower than the 100 ug/L drinking water standard unless extreme treatment plant conditions exist. Managers should be aware of these extremes and try to keep treatment plants operating under typical conditions.

Justification for discontinuing the use of chlorine disinfection at AF WWTPs cannot be based on this research. The values of THMFP predicted for wastewater chlorination practices is too low to cause the AF to consider eliminating chlorine usage

or to justify the expense of de-chlorination equipment. Although this research does not support these major changes in disinfection practices, many states are beginning to mandate dechlorination or the use of an alternative disinfectant. Based on this research, the beneficial properties of chlorine disinfection outweigh the potentially damaging effects of the minimal DBPs formed.

APPENDIX A:

Data Survey Examples



DEPARTMENT OF THE AIR FORCE

AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY
WRIGHT-PATTERSON AIR FORCE BASE, OHIO


100 100 1004

MEMORANDUM FOR ENVIRONMENTAL FLIGHTS (see distribution)
ATTENTION: Compliance Managers

FROM: AFIT/ENV
Box 4366
2950 P Street
Wright Patterson AFB OH 45433-7765

SUBJECT: Collection of Environmental Compliance Data

1. The Air Force Institute of Technology is in a unique position to address many of the challenges facing today's Air Force. One such challenge is the Air Force's goal to reach total environmental compliance. Capt David Piech, who is presently enrolled in AFIT's Engineering and Environmental Management masters degree program, is researching alternative methods of disinfecting effluent from wastewater treatment plants (WWTP).
2. Capt Piech's research is directed toward comparing the alternatives available to the chlorination of effluent from Air Force WWTPs. He is attempting to develop a decision making tool that can be used to select the most cost effective and efficient method of disinfecting WWTP effluents. To do this, he needs some data that is not tracked by your MAJCOM which addresses your base's treatment of wastewater. This promising research could provide an outline for selecting an alternative to the use of chlorine for the disinfection of WWTP effluent.
3. Attached is a questionnaire pertaining to specific operations and limitations for the operation of WWTPs. Please fill out this data sheet and return it to Capt Piech at the above address or fax it to him at DSN 986-7302 by 6 May 94. We greatly appreciate your assistance with this research effort. You are participating in a critical step of an effort that will pay great dividends in the Air Force's future.


Michael L. Shelley, Lt Col, USAF, BSC
Head, Department of Engineering and
Environmental Management

Attachment:
WWTP Data Sheet

DISTRIBUTION:
See Attached

Name of Installation_____.

Name and Position of Individual Completing this Questionnaire_____

_____.

DSN_____.

Does your installation operate a wastewater treatment plant? Yes No
(If No please stop here and return questionnaire.)

Type of treatment plant (i.e. Primary, Secondary etc.)_____

Please briefly describe plant operations._____

_____.

Method of disinfection (i.e. Chlorination, Ozone, Ultra Violet)_____.

If Chlorination, do you dechlorinate? Yes No

If yes, what method is used?_____.

Average Amount of Chlorine Used Per Day_____.

Maximum Design Flow_____.

Average Daily Flow_____.

Continued on Next Page...

	<u>Permit Limitations</u>	<u>Monthly Average</u>
Total Coliforms	_____	_____
Suspended Solids	_____	_____
Ammonia-Nitrogen	_____	_____
Turbidity	_____	_____
Chlorine Residual	_____	_____
BOD	_____	_____

Effluent is discharged to_____
(i.e. River, Stream, etc. and Specific Name of Receiving Body)

Has your WWTP ever experienced a trihalomethane problem with the effluent or the receiving body that the effluent is discharged to?_____.

(If so, please briefly explain)_____

_____.

Please add any specific requirements or operations pertaining to disinfection that are enforced by a regulatory agency.

Reply to

Attn of:

Capt Carol McCormick
AFIT/ENV Box 4385
WPAFB, OH

16 June, 1994

Subj: Waste Water Treatment Plant Data

To: Msgt Robert Ermes

1. This letter is in thanks for all the help you have given Capt Dave Piech and myself on our thesis research to date and to request additional data to support my waste water research project. My research involves the modeling of total organic halogens formed from chlorinating waste water. I am trying to determine whether or not the Air Force adds a significant amount of disinfection by-products to the receiving streams we release to. Because your WWTP uses chlorine for disinfection purposes I am requesting additional information from you.

2. I am requesting the following data on your effluent after passing through the chlorine contact chamber:

Total Organic Carbon = nonpurgeable organic carbon in mg/L _____
UV absorbance = 1-cm path length, 254 nm, and pH 7 _____
Average temperature of effluent _____
Average pH of effluent _____
Applied chlorine dose in mg as Cl_2/L _____
Reaction time in chlorine chamber _____
Dimensions of chlorine contact chamber _____
Bromide concentration in mg/L _____
Total Trihalomethane (THM) concentration in mg/L _____

And one measurement from before the chamber: Total THM in mg/L _____

3. Any amount of information you can give me will help, but if the effort can be made to gather all the data, my research will be a valid input to the effort to upgrade Air Force WWTPs in the future. Please FAX answers back to AFIT at DSN 986-7302 or (513) 476-7302.

4 Thank you in advance for any of the help you can give me in gathering this baseline data. I truly appreciate the effort you are making to help us graduate. Please call me if there are any questions (513)429-2724 or voice mail 255-3636 x1304.

-S-

CAROL ANN MCCORMICK
Capt, USAF

APPENDIX B:

Model Predictions for Typical WWTP Characteristics

THM Formation Potential (Chlorine Dose at 10 mg/L)

TOC in mg/L	THM Formation in ug/L
5.00	38.00
6.00	41.00
7.00	44.00
8.00	47.00
9.00	50.00
10.00	53.00
11.00	56.00
12.00	59.00
13.00	62.00
14.00	65.00
15.00	68.00
16.00	71.00
17.00	74.00
18.00	77.00
19.00	80.00
20.00	83.00
21.00	86.00
22.00	89.00
23.00	92.00
24.00	95.00
25.00	98.00
26.00	101.00
27.00	104.00
28.00	107.00
29.00	110.00
30.00	113.00

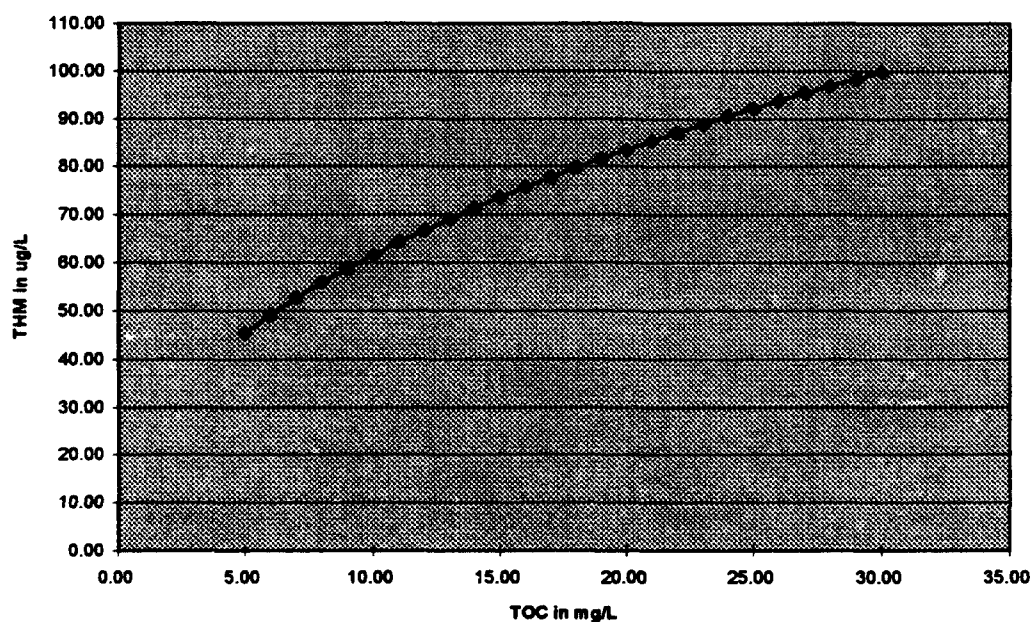
MODEL2.XLS

THM Formation based on Log-Log Recalibrated Model

Variable = Chlorine Dose of 15.0 mg/L Constant = Reaction Time of .5 hours, Temperature of 20 degrees C.

TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L
5.00	0.07	15.00	20	0.50	0.01	7	0.34	45.42
6.00	0.07	15.00	20	0.50	0.01	7	0.37	49.21
7.00	0.07	15.00	20	0.50	0.01	7	0.39	52.66
8.00	0.07	15.00	20	0.50	0.01	7	0.42	55.85
9.00	0.07	15.00	20	0.50	0.01	7	0.44	58.82
10.00	0.07	15.00	20	0.50	0.01	7	0.46	61.61
11.00	0.07	15.00	20	0.50	0.01	7	0.48	64.25
12.00	0.07	15.00	20	0.50	0.01	7	0.50	66.76
13.00	0.07	15.00	20	0.50	0.01	7	0.52	69.15
14.00	0.07	15.00	20	0.50	0.01	7	0.53	71.44
15.00	0.07	15.00	20	0.50	0.01	7	0.55	73.64
16.00	0.07	15.00	20	0.50	0.01	7	0.57	75.76
17.00	0.07	15.00	20	0.50	0.01	7	0.58	77.81
18.00	0.07	15.00	20	0.50	0.01	7	0.60	79.79
19.00	0.07	15.00	20	0.50	0.01	7	0.61	81.72
20.00	0.07	15.00	20	0.50	0.01	7	0.62	83.58
21.00	0.07	15.00	20	0.50	0.01	7	0.64	85.39
22.00	0.07	15.00	20	0.50	0.01	7	0.65	87.16
23.00	0.07	15.00	20	0.50	0.01	7	0.66	88.88
24.00	0.07	15.00	20	0.50	0.01	7	0.68	90.56
25.00	0.07	15.00	20	0.50	0.01	7	0.69	92.20
26.00	0.07	15.00	20	0.50	0.01	7	0.70	93.81
27.00	0.07	15.00	20	0.50	0.01	7	0.71	95.38
28.00	0.07	15.00	20	0.50	0.01	7	0.72	96.92
29.00	0.07	15.00	20	0.50	0.01	7	0.73	98.43
30.00	0.07	15.00	20	0.50	0.01	7	0.75	99.91

THM Formation Potential (Chlorine Dose at 15 mg/L)



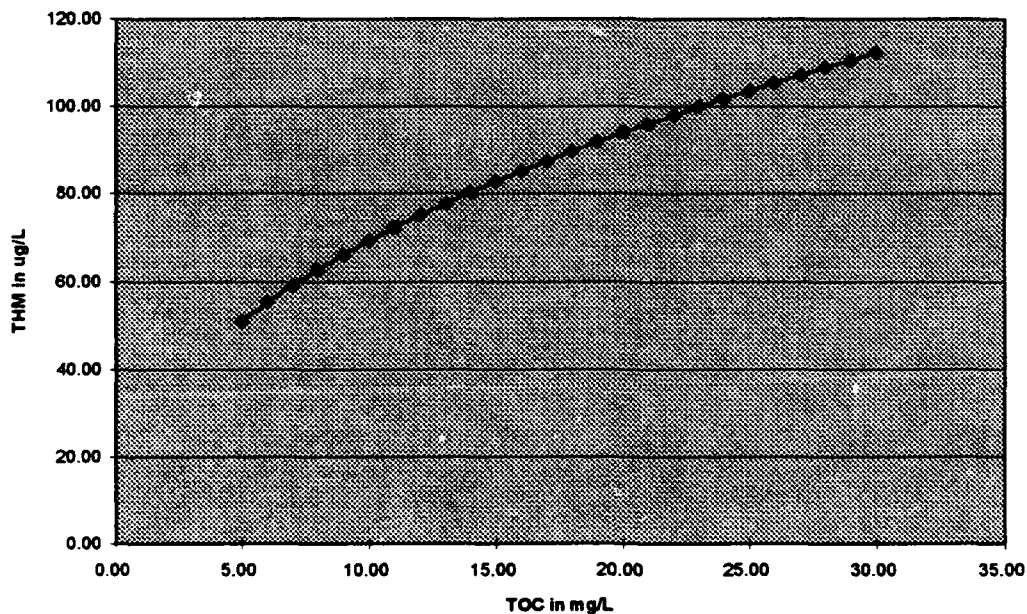
MODEL2.XLS

THM Formation based on Log-Log Recalibrated Model

Variable = Chlorine Dose of 20.0 mg/L Constant = Reaction Time of .5 hours, Temperature of 20 degrees C.

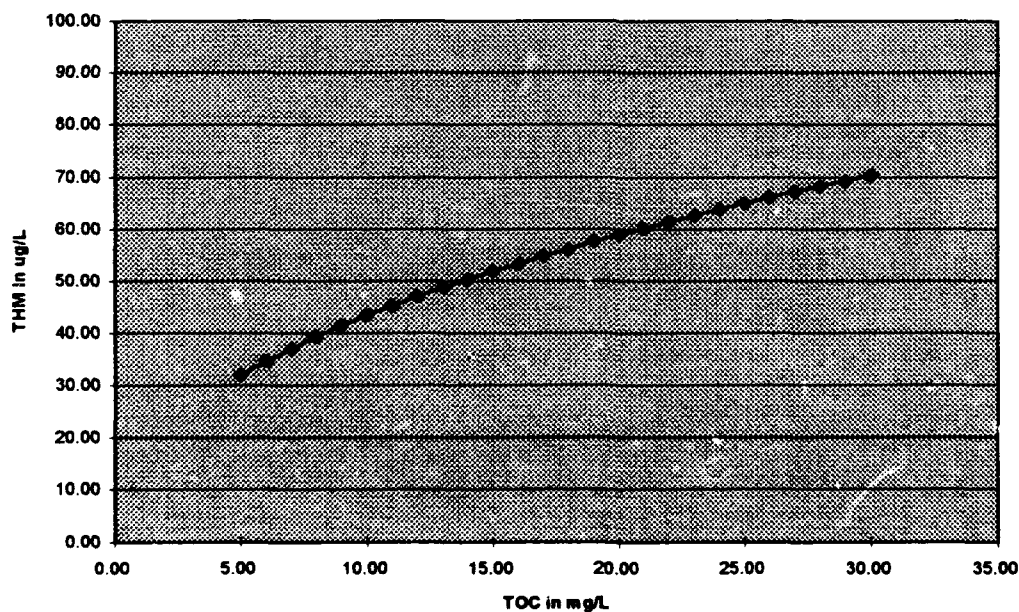
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L
5.00	0.07	20.00	20	0.50	0.01	7	0.38	51.09
6.00	0.07	20.00	20	0.50	0.01	7	0.41	55.35
7.00	0.07	20.00	20	0.50	0.01	7	0.44	59.24
8.00	0.07	20.00	20	0.50	0.01	7	0.47	62.82
9.00	0.07	20.00	20	0.50	0.01	7	0.49	66.16
10.00	0.07	20.00	20	0.50	0.01	7	0.52	69.30
11.00	0.07	20.00	20	0.50	0.01	7	0.54	72.27
12.00	0.07	20.00	20	0.50	0.01	7	0.56	75.09
13.00	0.07	20.00	20	0.50	0.01	7	0.58	77.78
14.00	0.07	20.00	20	0.50	0.01	7	0.60	80.36
15.00	0.07	20.00	20	0.50	0.01	7	0.62	82.84
16.00	0.07	20.00	20	0.50	0.01	7	0.64	85.22
17.00	0.07	20.00	20	0.50	0.01	7	0.65	87.53
18.00	0.07	20.00	20	0.50	0.01	7	0.67	89.76
19.00	0.07	20.00	20	0.50	0.01	7	0.69	91.92
20.00	0.07	20.00	20	0.50	0.01	7	0.70	94.02
21.00	0.07	20.00	20	0.50	0.01	7	0.72	96.06
22.00	0.07	20.00	20	0.50	0.01	7	0.73	98.04
23.00	0.07	20.00	20	0.50	0.01	7	0.75	99.98
24.00	0.07	20.00	20	0.50	0.01	7	0.76	101.87
25.00	0.07	20.00	20	0.50	0.01	7	0.77	103.72
26.00	0.07	20.00	20	0.50	0.01	7	0.79	105.52
27.00	0.07	20.00	20	0.50	0.01	7	0.80	107.29
28.00	0.07	20.00	20	0.50	0.01	7	0.81	109.02
29.00	0.07	20.00	20	0.50	0.01	7	0.83	110.72
30.00	0.07	20.00	20	0.50	0.01	7	0.84	112.38

THM Formation Potential (Chlorine Dose at 20 mg/L)



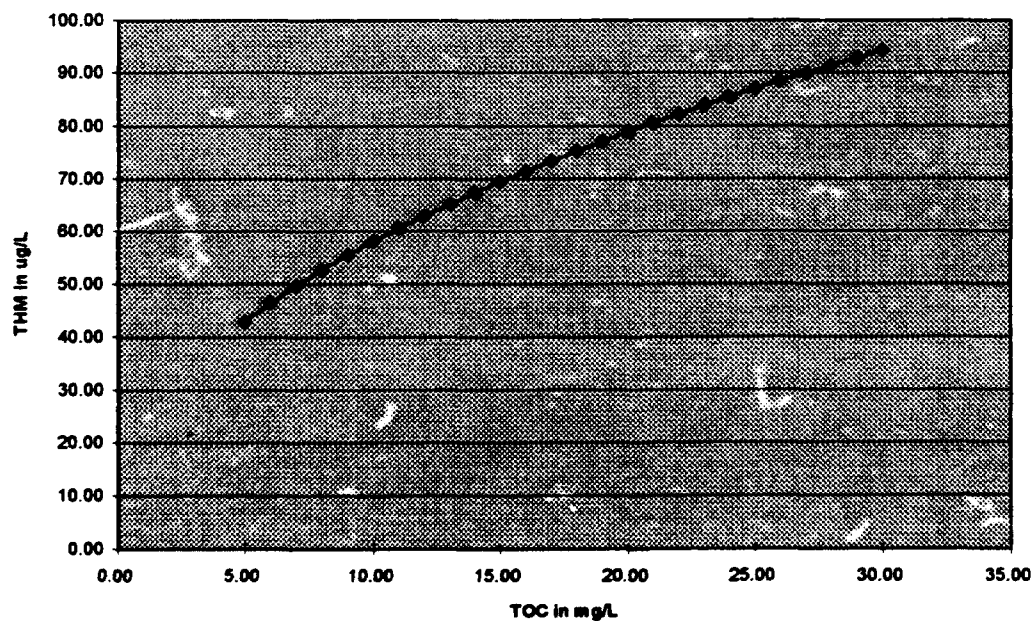
MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = Reaction Time of .25 hours				Constant = Chlorine Dose of 10 mg/L, Temperature of 20 degrees C.					
TOC mg/L	UVABS cm-1	CLDOSE mg	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L	
5.00	0.07	10.00	20	0.25	0.01	7	0.24	32.02	
6.00	0.07	10.00	20	0.25	0.01	7	0.26	34.69	
7.00	0.07	10.00	20	0.25	0.01	7	0.28	37.13	
8.00	0.07	10.00	20	0.25	0.01	7	0.29	39.37	
9.00	0.07	10.00	20	0.25	0.01	7	0.31	41.47	
10.00	0.07	10.00	20	0.25	0.01	7	0.32	43.44	
11.00	0.07	10.00	20	0.25	0.01	7	0.34	45.30	
12.00	0.07	10.00	20	0.25	0.01	7	0.35	47.07	
13.00	0.07	10.00	20	0.25	0.01	7	0.36	48.75	
14.00	0.07	10.00	20	0.25	0.01	7	0.38	50.37	
15.00	0.07	10.00	20	0.25	0.01	7	0.39	51.92	
16.00	0.07	10.00	20	0.25	0.01	7	0.40	53.42	
17.00	0.07	10.00	20	0.25	0.01	7	0.41	54.86	
18.00	0.07	10.00	20	0.25	0.01	7	0.42	56.26	
19.00	0.07	10.00	20	0.25	0.01	7	0.43	57.61	
20.00	0.07	10.00	20	0.25	0.01	7	0.44	58.93	
21.00	0.07	10.00	20	0.25	0.01	7	0.45	60.21	
22.00	0.07	10.00	20	0.25	0.01	7	0.46	61.45	
23.00	0.07	10.00	20	0.25	0.01	7	0.47	62.66	
24.00	0.07	10.00	20	0.25	0.01	7	0.48	63.85	
25.00	0.07	10.00	20	0.25	0.01	7	0.48	65.01	
26.00	0.07	10.00	20	0.25	0.01	7	0.49	66.14	
27.00	0.07	10.00	20	0.25	0.01	7	0.50	67.24	
28.00	0.07	10.00	20	0.25	0.01	7	0.51	68.33	
29.00	0.07	10.00	20	0.25	0.01	7	0.52	69.39	
30.00	0.07	10.00	20	0.25	0.01	7	0.53	70.44	

THM Formation Potential (Reaction Time of .25 hours)



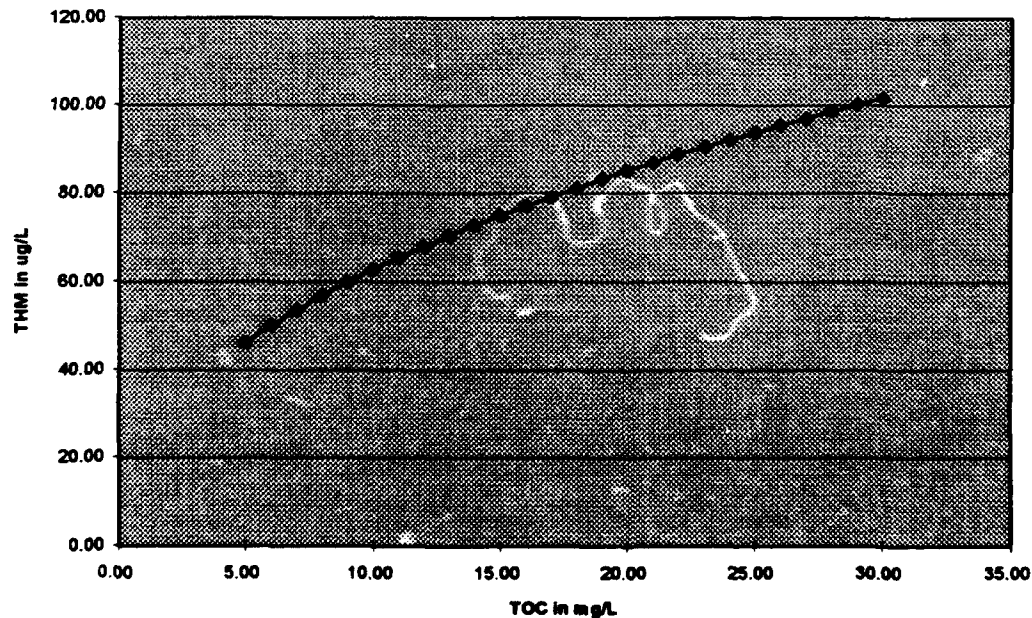
MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = Reaction Time of .75 hours				Constant = Chlorine Dose of 10 mg/L, Temperature of 20 degrees C.					
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L	
5.00	0.07	10.00	20	0.75	0.01	7	0.32	42.84	
6.00	0.07	10.00	20	0.75	0.01	7	0.35	46.42	
7.00	0.07	10.00	20	0.75	0.01	7	0.37	49.68	
8.00	0.07	10.00	20	0.75	0.01	7	0.39	52.68	
9.00	0.07	10.00	20	0.75	0.01	7	0.41	55.48	
10.00	0.07	10.00	20	0.75	0.01	7	0.43	58.12	
11.00	0.07	10.00	20	0.75	0.01	7	0.45	60.61	
12.00	0.07	10.00	20	0.75	0.01	7	0.47	62.97	
13.00	0.07	10.00	20	0.75	0.01	7	0.49	65.23	
14.00	0.07	10.00	20	0.75	0.01	7	0.50	67.39	
15.00	0.07	10.00	20	0.75	0.01	7	0.52	69.47	
16.00	0.07	10.00	20	0.75	0.01	7	0.53	71.47	
17.00	0.07	10.00	20	0.75	0.01	7	0.55	73.40	
18.00	0.07	10.00	20	0.75	0.01	7	0.56	75.27	
19.00	0.07	10.00	20	0.75	0.01	7	0.57	77.08	
20.00	0.07	10.00	20	0.75	0.01	7	0.59	78.84	
21.00	0.07	10.00	20	0.75	0.01	7	0.60	80.55	
22.00	0.07	10.00	20	0.75	0.01	7	0.61	82.22	
23.00	0.07	10.00	20	0.75	0.01	7	0.63	83.84	
24.00	0.07	10.00	20	0.75	0.01	7	0.64	85.43	
25.00	0.07	10.00	20	0.75	0.01	7	0.65	86.97	
26.00	0.07	10.00	20	0.75	0.01	7	0.66	88.49	
27.00	0.07	10.00	20	0.75	0.01	7	0.67	89.97	
28.00	0.07	10.00	20	0.75	0.01	7	0.68	91.42	
29.00	0.07	10.00	20	0.75	0.01	7	0.69	92.84	
30.00	0.07	10.00	20	0.75	0.01	7	0.70	94.24	

THM Formation Potential (Reaction Time of .75 hours)

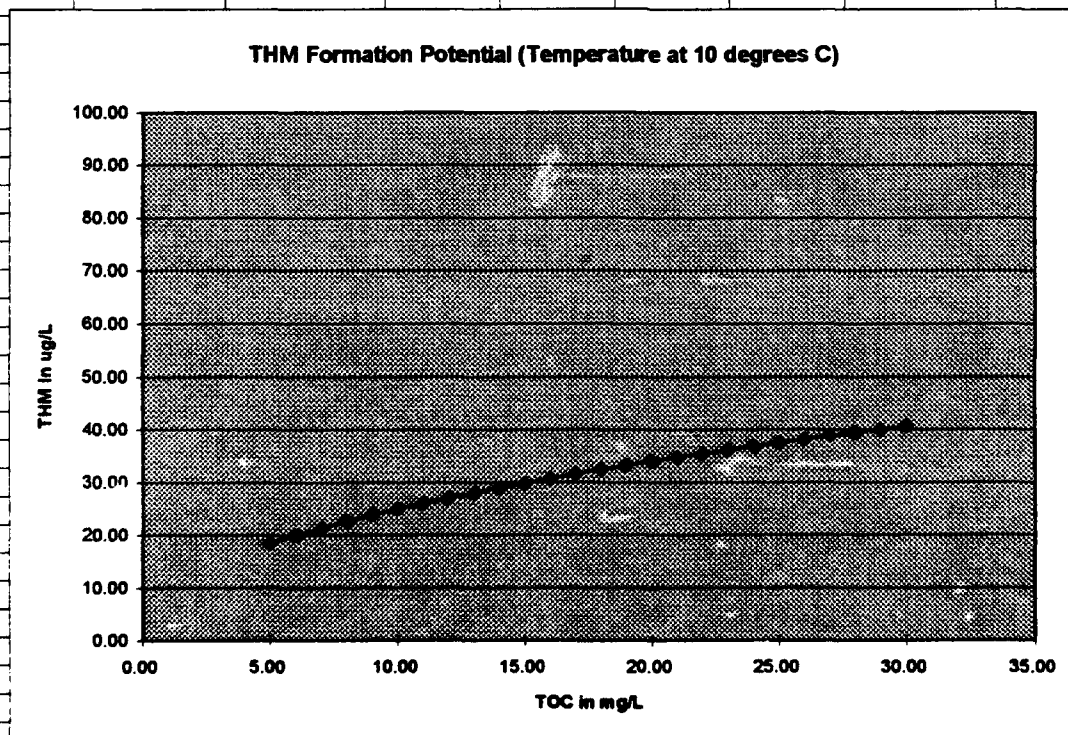


MODEL2.XLS								
THM Formation based on Log-Log Recalibrated Model								
Variable = Reaction Time of 1 hour			Constant = Chlorine Dose of 10 mg/L, Temperature of 20 degrees C.					
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L
5.00	0.07	10.00	20	1.00	0.01	7	0.34	46.23
6.00	0.07	10.00	20	1.00	0.01	7	0.37	50.09
7.00	0.07	10.00	20	1.00	0.01	7	0.40	53.61
8.00	0.07	10.00	20	1.00	0.01	7	0.42	56.85
9.00	0.07	10.00	20	1.00	0.01	7	0.45	59.88
10.00	0.07	10.00	20	1.00	0.01	7	0.47	62.72
11.00	0.07	10.00	20	1.00	0.01	7	0.49	65.41
12.00	0.07	10.00	20	1.00	0.01	7	0.51	67.96
13.00	0.07	10.00	20	1.00	0.01	7	0.53	70.39
14.00	0.07	10.00	20	1.00	0.01	7	0.54	72.73
15.00	0.07	10.00	20	1.00	0.01	7	0.56	74.97
16.00	0.07	10.00	20	1.00	0.01	7	0.58	77.13
17.00	0.07	10.00	20	1.00	0.01	7	0.59	79.21
18.00	0.07	10.00	20	1.00	0.01	7	0.61	81.23
19.00	0.07	10.00	20	1.00	0.01	7	0.62	83.19
20.00	0.07	10.00	20	1.00	0.01	7	0.63	85.09
21.00	0.07	10.00	20	1.00	0.01	7	0.65	86.93
22.00	0.07	10.00	20	1.00	0.01	7	0.66	88.73
23.00	0.07	10.00	20	1.00	0.01	7	0.67	90.48
24.00	0.07	10.00	20	1.00	0.01	7	0.69	92.19
25.00	0.07	10.00	20	1.00	0.01	7	0.70	93.86
26.00	0.07	10.00	20	1.00	0.01	7	0.71	95.50
27.00	0.07	10.00	20	1.00	0.01	7	0.72	97.10
28.00	0.07	10.00	20	1.00	0.01	7	0.74	98.66
29.00	0.07	10.00	20	1.00	0.01	7	0.75	100.20
30.00	0.07	10.00	20	1.00	0.01	7	0.76	101.70

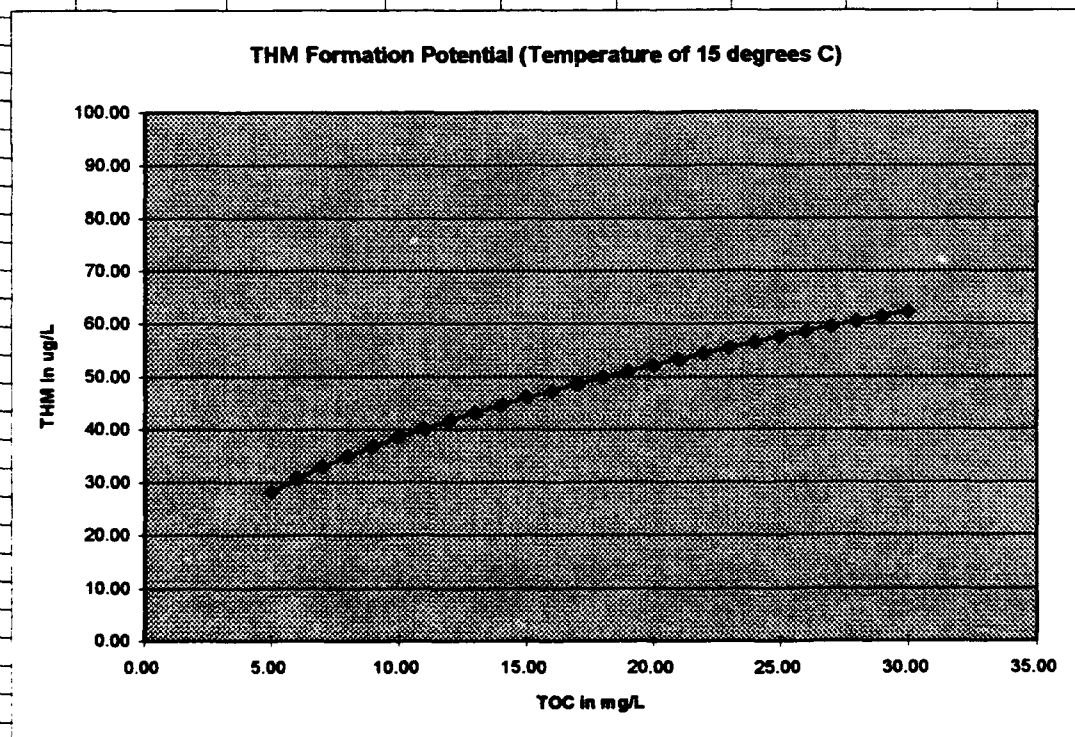
THM Formation Potential (Reaction Time of 1 hour)



MODEL2.XLS								
THM Formation based on Log-Log Recalibrated Model								
Variable = Temperature of 10 degrees C.			Constant = Reaction Time of .5 hours, Chlorine Dose of 10 mg/L.					
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L
5.00	0.07	10.00	10	0.50	0.01	7	0.14	18.45
6.00	0.07	10.00	10	0.50	0.01	7	0.15	20.00
7.00	0.07	10.00	10	0.50	0.01	7	0.16	21.40
8.00	0.07	10.00	10	0.50	0.01	7	0.17	22.69
9.00	0.07	10.00	10	0.50	0.01	7	0.18	23.90
10.00	0.07	10.00	10	0.50	0.01	7	0.19	25.03
11.00	0.07	10.00	10	0.50	0.01	7	0.19	26.11
12.00	0.07	10.00	10	0.50	0.01	7	0.20	27.13
13.00	0.07	10.00	10	0.50	0.01	7	0.21	28.10
14.00	0.07	10.00	10	0.50	0.01	7	0.22	29.03
15.00	0.07	10.00	10	0.50	0.01	7	0.22	29.92
16.00	0.07	10.00	10	0.50	0.01	7	0.23	30.79
17.00	0.07	10.00	10	0.50	0.01	7	0.24	31.62
18.00	0.07	10.00	10	0.50	0.01	7	0.24	32.42
19.00	0.07	10.00	10	0.50	0.01	7	0.25	33.20
20.00	0.07	10.00	10	0.50	0.01	7	0.25	33.96
21.00	0.07	10.00	10	0.50	0.01	7	0.26	34.70
22.00	0.07	10.00	10	0.50	0.01	7	0.26	35.42
23.00	0.07	10.00	10	0.50	0.01	7	0.27	36.12
24.00	0.07	10.00	10	0.50	0.01	7	0.27	36.80
25.00	0.07	10.00	10	0.50	0.01	7	0.28	37.47
26.00	0.07	10.00	10	0.50	0.01	7	0.28	38.12
27.00	0.07	10.00	10	0.50	0.01	7	0.29	38.76
28.00	0.07	10.00	10	0.50	0.01	7	0.29	39.38
29.00	0.07	10.00	10	0.50	0.01	7	0.30	39.99
30.00	0.07	10.00	10	0.50	0.01	7	0.30	40.60

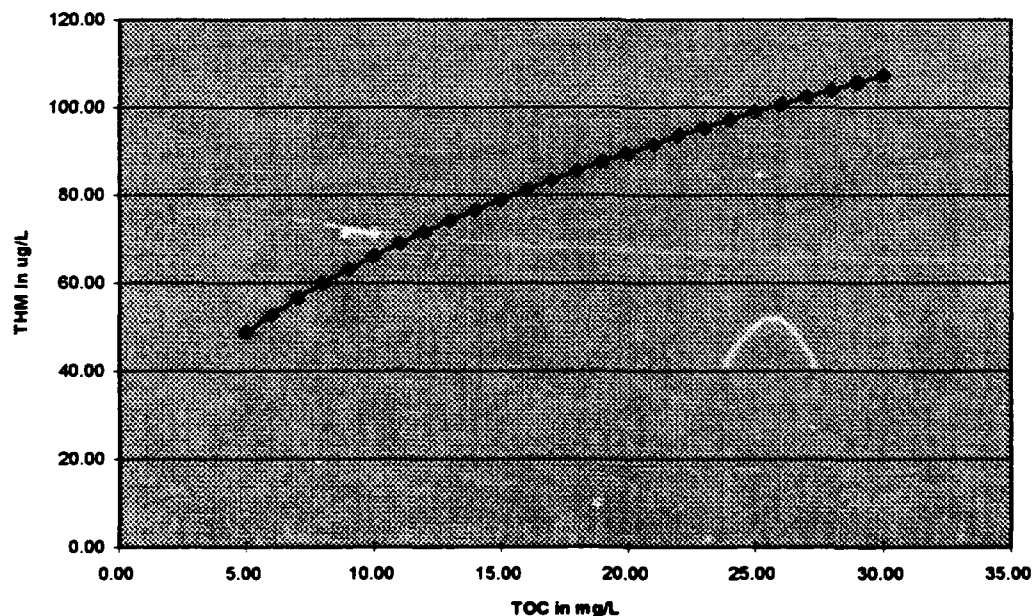


MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = Temperature at 15 degrees C. Constant = Reaction Time of .5 hours, Chlorine Dose of 10 mg/L.									
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L	
5.00	0.07	10.00	15	0.50	0.01	7	0.21	28.36	
6.00	0.07	10.00	15	0.50	0.01	7	0.23	30.73	
7.00	0.07	10.00	15	0.50	0.01	7	0.25	32.89	
8.00	0.07	10.00	15	0.50	0.01	7	0.26	34.88	
9.00	0.07	10.00	15	0.50	0.01	7	0.27	36.73	
10.00	0.07	10.00	15	0.50	0.01	7	0.29	38.48	
11.00	0.07	10.00	15	0.50	0.01	7	0.30	40.12	
12.00	0.07	10.00	15	0.50	0.01	7	0.31	41.69	
13.00	0.07	10.00	15	0.50	0.01	7	0.32	43.18	
14.00	0.07	10.00	15	0.50	0.01	7	0.33	44.62	
15.00	0.07	10.00	15	0.50	0.01	7	0.34	45.99	
16.00	0.07	10.00	15	0.50	0.01	7	0.35	47.32	
17.00	0.07	10.00	15	0.50	0.01	7	0.36	48.60	
18.00	0.07	10.00	15	0.50	0.01	7	0.37	49.83	
19.00	0.07	10.00	15	0.50	0.01	7	0.38	51.03	
20.00	0.07	10.00	15	0.50	0.01	7	0.39	52.20	
21.00	0.07	10.00	15	0.50	0.01	7	0.40	53.33	
22.00	0.07	10.00	15	0.50	0.01	7	0.41	54.43	
23.00	0.07	10.00	15	0.50	0.01	7	0.41	55.51	
24.00	0.07	10.00	15	0.50	0.01	7	0.42	56.56	
25.00	0.07	10.00	15	0.50	0.01	7	0.43	57.58	
26.00	0.07	10.00	15	0.50	0.01	7	0.44	58.58	
27.00	0.07	10.00	15	0.50	0.01	7	0.44	59.57	
28.00	0.07	10.00	15	0.50	0.01	7	0.45	60.53	
29.00	0.07	10.00	15	0.50	0.01	7	0.46	61.47	
30.00	0.07	10.00	15	0.50	0.01	7	0.47	62.39	

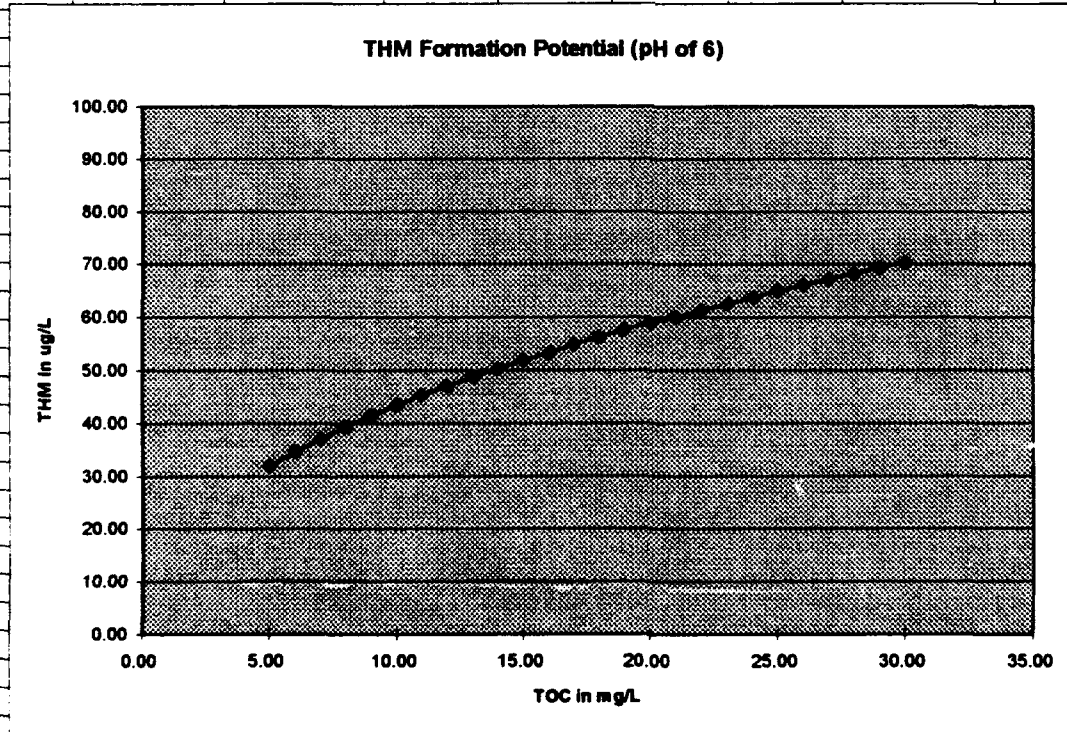


MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = Temperature of 25 degrees C.				Constant = Reaction Time of .5 hours, Chlorine Dose of 10 mg/L.					
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM u.no/L	TTHM ug/L	
5.00	0.07	10.00	25	0.50	0.01	7	0.36	48.74	
6.00	0.07	10.00	25	0.50	0.01	7	0.39	52.81	
7.00	0.07	10.00	25	0.50	0.01	7	0.42	56.52	
8.00	0.07	10.00	25	0.50	0.01	7	0.45	59.94	
9.00	0.07	10.00	25	0.50	0.01	7	0.47	63.13	
10.00	0.07	10.00	25	0.50	0.01	7	0.49	66.12	
11.00	0.07	10.00	25	0.50	0.01	7	0.51	68.96	
12.00	0.07	10.00	25	0.50	0.01	7	0.53	71.65	
13.00	0.07	10.00	25	0.50	0.01	7	0.55	74.22	
14.00	0.07	10.00	25	0.50	0.01	7	0.57	76.67	
15.00	0.07	10.00	25	0.50	0.01	7	0.59	79.04	
16.00	0.07	10.00	25	0.50	0.01	7	0.61	81.31	
17.00	0.07	10.00	25	0.50	0.01	7	0.62	83.51	
18.00	0.07	10.00	25	0.50	0.01	7	0.64	85.64	
19.00	0.07	10.00	25	0.50	0.01	7	0.65	87.70	
20.00	0.07	10.00	25	0.50	0.01	7	0.67	89.70	
21.00	0.07	10.00	25	0.50	0.01	7	0.68	91.65	
22.00	0.07	10.00	25	0.50	0.01	7	0.70	93.55	
23.00	0.07	10.00	25	0.50	0.01	7	0.71	95.39	
24.00	0.07	10.00	25	0.50	0.01	7	0.73	97.20	
25.00	0.07	10.00	25	0.50	0.01	7	0.74	98.96	
26.00	0.07	10.00	25	0.50	0.01	7	0.75	100.68	
27.00	0.07	10.00	25	0.50	0.01	7	0.76	102.37	
28.00	0.07	10.00	25	0.50	0.01	7	0.78	104.02	
29.00	0.07	10.00	25	0.50	0.01	7	0.79	105.64	
30.00	0.07	10.00	25	0.50	0.01	7	0.80	107.22	

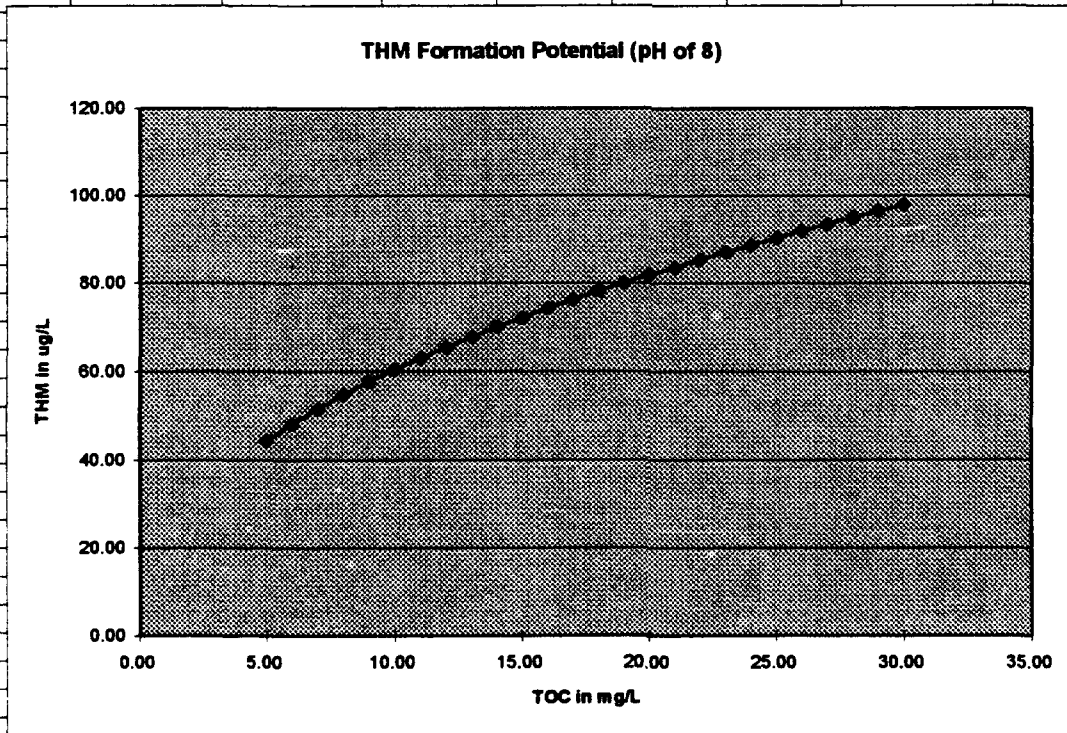
THM Formation Potential (Temperature at 25 degrees C)



MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = pH of 6		Constant = Reaction Time of .5 hours, Temperature of 20 degrees C, Chlorine Dose of 10 mg/L.							
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L	
5.00	0.07	10.00	20	0.50	0.01	6	0.24	32.00	
6.00	0.07	10.00	20	0.50	0.01	6	0.26	34.67	
7.00	0.07	10.00	20	0.50	0.01	6	0.28	37.10	
8.00	0.07	10.00	20	0.50	0.01	6	0.29	39.35	
9.00	0.07	10.00	20	0.50	0.01	6	0.31	41.44	
10.00	0.07	10.00	20	0.50	0.01	6	0.32	43.41	
11.00	0.07	10.00	20	0.50	0.01	6	0.34	45.27	
12.00	0.07	10.00	20	0.50	0.01	6	0.35	47.03	
13.00	0.07	10.00	20	0.50	0.01	6	0.36	48.72	
14.00	0.07	10.00	20	0.50	0.01	6	0.38	50.33	
15.00	0.07	10.00	20	0.50	0.01	6	0.39	51.89	
16.00	0.07	10.00	20	0.50	0.01	6	0.40	53.38	
17.00	0.07	10.00	20	0.50	0.01	6	0.41	54.82	
18.00	0.07	10.00	20	0.50	0.01	6	0.42	56.22	
19.00	0.07	10.00	20	0.50	0.01	6	0.43	57.57	
20.00	0.07	10.00	20	0.50	0.01	6	0.44	58.89	
21.00	0.07	10.00	20	0.50	0.01	6	0.45	60.17	
22.00	0.07	10.00	20	0.50	0.01	6	0.46	61.41	
23.00	0.07	10.00	20	0.50	0.01	6	0.47	62.62	
24.00	0.07	10.00	20	0.50	0.01	6	0.48	63.81	
25.00	0.07	10.00	20	0.50	0.01	6	0.48	64.96	
26.00	0.07	10.00	20	0.50	0.01	6	0.49	66.09	
27.00	0.07	10.00	20	0.50	0.01	6	0.50	67.20	
28.00	0.07	10.00	20	0.50	0.01	6	0.51	68.28	
29.00	0.07	10.00	20	0.50	0.01	6	0.52	69.35	
30.00	0.07	10.00	20	0.50	0.01	6	0.53	70.39	

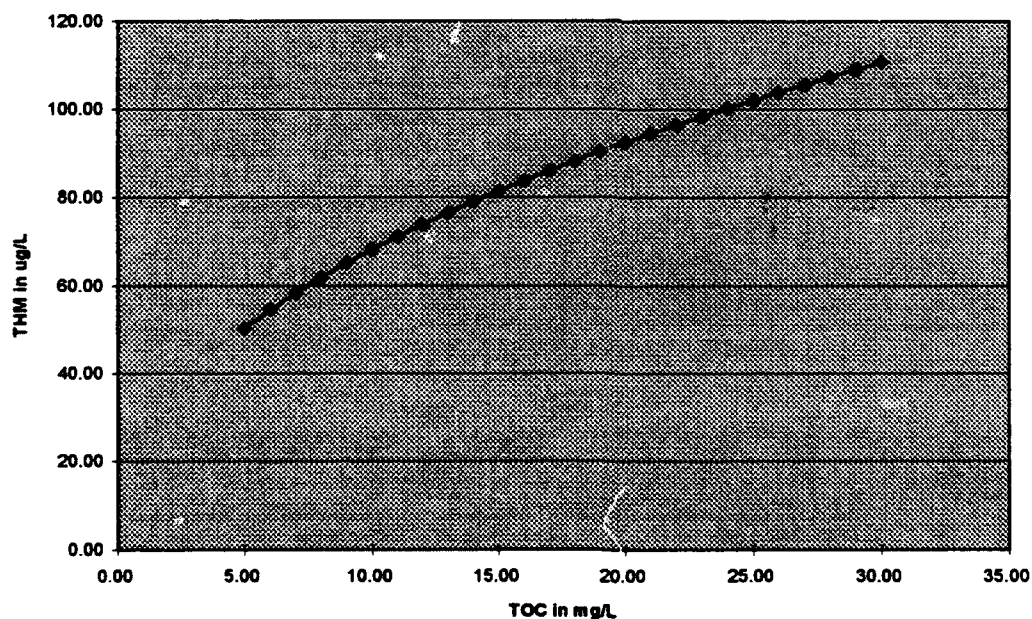


MODEL2.XLS									
THM Formation based on Log-Log Recalibrated Model									
Variable = pH of 8 Constant = Reaction Time of .5 hours, Temperature of 20 degrees C, Chlorine Dose of 10 mg/L.									
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L	
5.00	0.07	10.00	20	0.50	0.01	8	0.33	44.54	
6.00	0.07	10.00	20	0.50	0.01	8	0.36	48.26	
7.00	0.07	10.00	20	0.50	0.01	8	0.39	51.65	
8.00	0.07	10.00	20	0.50	0.01	8	0.41	54.78	
9.00	0.07	10.00	20	0.50	0.01	8	0.43	57.69	
10.00	0.07	10.00	20	0.50	0.01	8	0.45	60.43	
11.00	0.07	10.00	20	0.50	0.01	8	0.47	63.01	
12.00	0.07	10.00	20	0.50	0.01	8	0.49	65.47	
13.00	0.07	10.00	20	0.50	0.01	8	0.51	67.82	
14.00	0.07	10.00	20	0.50	0.01	8	0.52	70.07	
15.00	0.07	10.00	20	0.50	0.01	8	0.54	72.23	
16.00	0.07	10.00	20	0.50	0.01	8	0.55	74.31	
17.00	0.07	10.00	20	0.50	0.01	8	0.57	76.32	
18.00	0.07	10.00	20	0.50	0.01	8	0.58	78.26	
19.00	0.07	10.00	20	0.50	0.01	8	0.60	80.15	
20.00	0.07	10.00	20	0.50	0.01	8	0.61	81.97	
21.00	0.07	10.00	20	0.50	0.01	8	0.62	83.75	
22.00	0.07	10.00	20	0.50	0.01	8	0.64	85.49	
23.00	0.07	10.00	20	0.50	0.01	8	0.65	87.17	
24.00	0.07	10.00	20	0.50	0.01	8	0.66	88.82	
25.00	0.07	10.00	20	0.50	0.01	8	0.67	90.43	
26.00	0.07	10.00	20	0.50	0.01	8	0.69	92.01	
27.00	0.07	10.00	20	0.50	0.01	8	0.70	93.55	
28.00	0.07	10.00	20	0.50	0.01	8	0.71	95.06	
29.00	0.07	10.00	20	0.50	0.01	8	0.72	96.53	
30.00	0.07	10.00	20	0.50	0.01	8	0.73	97.98	



MODEL2.XLS								
THM Formation based on Log-Log Recalibrated Model								
Variable = pH of 9			Constant = Reaction Time of .5 hours, Temperature of 20 degrees C, Chlorine Dose of 10 mg/L.					
TOC mg/L	UVABS cm-1	CLDOSE mg/l	TEMP	RXNTM hr	BR mg/L	PH	TTHM umol/L	TTHM ug/L
5.00	0.07	10.00	20	0.50	0.01	9	0.38	50.30
6.00	0.07	10.00	20	0.50	0.01	9	0.41	54.50
7.00	0.07	10.00	20	0.50	0.01	9	0.44	58.32
8.00	0.07	10.00	20	0.50	0.01	9	0.46	61.85
9.00	0.07	10.00	20	0.50	0.01	9	0.49	65.14
10.00	0.07	10.00	20	0.50	0.01	9	0.51	68.23
11.00	0.07	10.00	20	0.50	0.01	9	0.53	71.15
12.00	0.07	10.00	20	0.50	0.01	9	0.55	73.93
13.00	0.07	10.00	20	0.50	0.01	9	0.57	76.58
14.00	0.07	10.00	20	0.50	0.01	9	0.59	79.12
15.00	0.07	10.00	20	0.50	0.01	9	0.61	81.56
16.00	0.07	10.00	20	0.50	0.01	9	0.63	83.91
17.00	0.07	10.00	20	0.50	0.01	9	0.64	86.17
18.00	0.07	10.00	20	0.50	0.01	9	0.66	88.37
19.00	0.07	10.00	20	0.50	0.01	9	0.68	90.50
20.00	0.07	10.00	20	0.50	0.01	9	0.69	92.56
21.00	0.07	10.00	20	0.50	0.01	9	0.71	94.57
22.00	0.07	10.00	20	0.50	0.01	9	0.72	96.53
23.00	0.07	10.00	20	0.50	0.01	9	0.73	98.43
24.00	0.07	10.00	20	0.50	0.01	9	0.75	100.29
25.00	0.07	10.00	20	0.50	0.01	9	0.76	102.11
26.00	0.07	10.00	20	0.50	0.01	9	0.77	103.89
27.00	0.07	10.00	20	0.50	0.01	9	0.79	105.63
28.00	0.07	10.00	20	0.50	0.01	9	0.80	107.33
29.00	0.07	10.00	20	0.50	0.01	9	0.81	109.00
30.00	0.07	10.00	20	0.50	0.01	9	0.83	110.64

THM Formation Potential (pH of 9)



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Vita

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1994		3. REPORT TYPE AND DATES COVERED Master's Thesis
4. TITLE AND SUBTITLE MODELING TRIHALOMETHANE FORMATION POTENTIAL FROM WASTEWATER CHLORINATION				5. FUNDING NUMBERS
6. AUTHOR(S) Carol A. McCormick, Captain, USAF				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Institute of Technology, WPAFB OH. 45433-6583				8. PERFORMING ORGANIZATION REPORT NUMBER AFTT/GEE/ENV/94S-14
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) <p>The deletion of federally mandated fecal coliform limits has led many states to review and modify their wastewater disinfection requirements. One issue in analyzing wastewater disinfection is the discharge of potentially carcinogenic halogenated organics formed during the chlorination process. This research investigates the formation of one class of the halogenated organics, the trihalomethanes. The applicability of using drinking water trihalomethane formation models for use with wastewater effluent is examined. Three models are compared for predictive capability by using measured trihalomethane values from previous research data.</p> <p>The results show that a previously developed model is applicable for use based on assumptions stated. Results provide environmental managers with worst case predictions for a range of wastewater treatment plant (WWTP) parameters. Predictions indicate that trihalomethane formation from the chlorination of wastewater is typically lower than the Safe Drinking Water Act trihalomethane standard of 100 ug/L.</p> <p>The worst case model predictions reach, and in certain extreme cases, pass the standard of 100 ug/L. This level of trihalomethanes formed is minimized if aeration of the receiving bodies of water occurs. Based on this research, the risk of forming trihalomethanes as disinfection by-products from chlorination do not outweigh the benefits gained from proper chlorine disinfection of effluent.</p>				
14. SUBJECT TERMS Wastewater, Wastewater Disinfection By-product Modeling, Trihalomethanes Chlorination By-products, Chemical Modeling				15. NUMBER OF PAGES 96
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	